ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

INVESTIGATION OF THE EFFECTS OF CHROME-TANNED LEATHER ADDITIVES IN NATURAL RUBBER AND STYRENE-BUTADIENE RUBBER

M.Sc. THESIS

Semih ŞAŞMAZ

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KROMLA TABAKLANMIŞ DERİ ATIKLARININ DOĞAL KAUÇUK VE STİREN-BÜTADİEN KAUÇUĞUNA ETKİSİNİN İNCELENMESİ

YÜKSEK LİSANS TEZİ

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Semih ŞAŞMAZ, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 515141022, successfully defended the thesis/dissertation entitled "INVESTIGATION OF THE EFFECTS OF CHROME-TANNED LEATHER ADDITIVES IN NATURAL RUBBER AND STYRENE-BUTADIENE RUBBER" which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my sisters,

FOREWORD

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ABBREVIATIONS

ASTM	: American Society for Testing and Materials
BET	: Brunauer, Emmett and Teller surface area determination
BR	: Butadiene Rubber
CB	: Carbon Black
CBS	: N-cyclohexyl-2-benzothiazol sulfonamide
CR	: Neoprene Rubber
CTL	: Chrome-Tanned Leather
DSC	: Differential Scanning Calorimeter
EPDM	: Ethylene-Propylene-Diene Mononer Rubber
EPM	: Ethylene-Propylene Mononer Rubber
IIR	: Butyl rubber
IPPD	: *N*-2-Propyl-*N'*-Phenyl-*p*-Phenylenediamine
IR	: Synthetic Isoprene Rubber
MDR	: Moving Die Rheometer
NBR	: Acrylonitrile-Butadiene Rubber
NR	: Natural Rubber
NRN	: Neutralized Natural Rubber
PEG	: Poly(ethylene glycol)
Q	: Silicon Rubber
SBR	: Styrene-Butadiene Rubber
SEM	: Scanning Electron Microscope
TGA	: Thermal Gravimetric Analysis
TMQ	: Poly(1,2-dihydro-2,2,4-trimethylquinoline)
TMTD	: Tetramethylthiuram Disulfide
UV	: Ultraviolet
ISO	: International Organization For Standardization

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INVESTIGATION OF THE EFFECTS OF CHROME-TANNED LEATHER WASTES IN NATURAL RUBBER AND STYRENE-BUTADIENE RUBBER

SUMMARY

Rubbery raw materials have widespread usage area among polymeric materials and show high performance properties such as high elasticity, good abrasion strength, and low permanent deformation. These properties can also be modified by adding various additives in also various ratios as for desired usage area. These high performance properties are provided by crosslinking. Raw rubbers do not include crosslinks however these crosslinks occurs after heat treatment under pressure this process is called *vulcanization* or *curing*.

Usually rubbers are classified as natural and synthetic rubbers. Natural rubber (NR) is more prominent the synthetic ones due to high performance properties. Most commonly used synthetic rubbers are styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR), ethylene-propylene-diene rubber (EPDM), chloroprene rubber (neoprene, CR), and silicone rubber (Q). SBR is the most common synthetic rubber in tire and rubber industries.

Commonly used rubbers are processed by compounding with various types of fillers and additives; material properties can be improved by various type and/or ratio of these auxiliary ingredients. Material cost can be reduced by adding filler. Filler incorporation can also improve the properties such as processability, tensile strength, and hardness if needed.

As analyzed the structure of leather, three dimensional crosslinked collagen fibers, keratin and oil are observed. Collagen structure that exists in leather can be made stable by tanning process due to prevent biologically and chemically degradation. Hence, physical and chemical properties of leather are enhanced and appearance of leather is improved.

Since negative effects of chrome-tanned leather (CTL) based wastes that are generated during leather goods manufacturing process to the environment, these wastes should be discarded or better should be utilized somehow. Due to leather particles have crosslinked collagen fibers in structure, basic physical properties show a similarity with rubber based materials so it was thought that using utilizing these wastes as additive for rubber compounds may be a good idea.

In this study, thermal, morphological and before-after aging (70 ^{o}C, 70 h) mechanical properties of NR, SBR and NR/SBR 50/50 blend based rubber compounds were studied by incorporating CTL particles in various ratios. Before adding CTL shavings to rubber compounds, they were dried in an oven at 80 ^{o}C for 6 hours. It was recorded that 77.6% of CTL additives had length changing between 500-2000

μm in sieve analysis results. To investigate the CTL on NR, SBR and NR/SBR, the compounds were prepared as including 0, 5, 10, 15 and 20 phr of CTL. All ingredients were mixed in laboratory-size banbury mixer approximately for 10 minutes and then laboratory-size two roll mill was used either to homogenize or to turn into plates. Differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) were used to investigate thermal properties of compounds. Curing peak enthalpies (ΔH_c) were obtained from DSC thermograms. Adding CTL into NR and NRN (that includes neutralized CTL additives by 1% ammonium solutions) increased ΔH_c, however ΔH_c values of SBR and NR/SBR were decreased by CTL incorporations.

Vulcanization behaviors of the compounds were determined at 160 ^oC by using moving die rheometer (MDR).Rheometer parameters such as minimum torque (M_L), maximum torque (M_H), scorch time (t_{s2}), optimum curing time ($t_{90)}$ (that is necessary to obtain 90% torque value between M_H-M_L) were recorded. Increasing leather content reduced curing time of rubber compounds. Curing times for NR and NRN compounds changed between 1.5 and 2 minutes, it was between 2 and 5 minutes for SBR compounds, and between 2 and 3 minutes for NR/SBR blend compounds. Density measurement instrument was used to decide the amount of the compound to put into present curing molds. Vulcanization process was operated at 160 ^oC and 140 bar pressure in a hydraulic press according to data obtained from DSC and MDR. Samples were prepared as plates and thicknesses were 2 mm and 6 mm. Samples were cut dumbbell shape for tensile test and trouser shape for tear test by using standard pattern. Tensile strength, elongation at break, tear strength values were recorded by universal testing machine. CTL affected tensile strength, elongation at break and tear strength values of NR and NRN based composites somewhat, however these values were enhanced for SBR and NR/SBR composites. Hardness values was determined by Shore A hardness measurement instrument. Abrasion resistance and compression set values were also studied.

Thermal gravimetric analyzer (TGA) instrument was used to analyze mass losses of compounds for different CTL incorporation ratios. Increasing leather content shifted degradation temperatures of the vulcanizates earlier and decreased residue amount after 400 ^oC.

Samples were treated by thermal aging at 70 ^oC and 70 h. The changings of mechanical properties of composites were studied after aging processes. As result, while the increment of CTL amount increased permanent deformation of NR based composites insignificantly, for SBR and NR/SBR based composites, the permanent deformation values after aging were increased more significantly.

When evaluated hardness test results, CTL had no effect on the changing of hardness values of composites during aging. In tear test results, it has been concluded that leather incorporation did not affect tear strength of NR based composites; however there was a less decrement in improved tear strength effect for SBR based composites after aging by increasing CTL content. This decrement was less for NR/SBR based composites. While tensile strengths of NR based composites decreased by CTL content before aging, tensile strengths of NR based composites increased by adding CTL after aging. Beside, CTL did not affect tensile strength values of SBR based composites before aging in spite of a decrement was seen on tensile strength values by increasing CTL amount after aging. For NR/SBR based composites, CTL did not have any effect on tensile strength values before and after

aging. Adding CTL decreased the decrement of elongation at break values of NR based composites after aging due to enhanced aging resistance by CTL. Also it was recorded that CTL reduced the elongation at break values after aging for SBR-CTL composites. A different trend was seen on NR/SBR-CTL composites, CTL did not change elongation at break values after aging significantly.

On the other hand, neutralization process of leather was also investigated on the characteristics of rubber/leather composites in NR based compounds. Same thermal, rheological and mechanical tests were applied to these composites that were untreated and neutralized.

KROMLA TABAKLANMIŞ DERİ ATIKLARININ DOĞAL KAUÇUK VE STİREN-BÜTADİEN KAUÇUĞUNA ETKİSİNİN İNCELENMESİ

ÖZET

Polimerik malzemeler arasında geniş bir yeri olan kauçuklar yüksek elastikiyet, iyi aşınma dayanımı, düşük deformasyon gibi performans açısından önemli özelliklerinin yanında içerisine katılan malzemelerin türü ve/veya malzemelerin oranları değiştirilerek çok çeşitli mekanik özellikler elde edilebildiğinden dolayı oldukça geniş bir kullanım alanına sahiptirler. Kauçuklar diğer polimerlere göre üstün olan bu özelliklerini yapılarında oluşan çapraz bağlarla sağlamaktadırlar. Ham halde bulunan kauçuklarda bu çapraz bağlar olmamakla birlikte ısı, basınç gibi etkilerle vulkanizasyon adı verilen işlemler gerçekleştirerek kauçukların yapılarında bu çapraz bağlar elde edilebilmektedir.

Genel olarak bakıldığında kauçuklar doğal ve sentetik olmak üzere iki ana gruba ayrılmaktadır. Doğal kauçuk (NR) sahip olduğu üstün özelliklerden dolayı diğer kauçuklara göre ön plana çıkmaktadır. En yaygın kullanılan sentetik kauçuklar stiren-bütadien kauçuğu (SBR), akrilonitril-bütadien kauçuğu (NBR), etilen-propilen-dien monomer kauçuğu (EPDM), kloropren kauçuğu (neopren, CR) ve silikon kauçuğudur (Q). Adı geçen sentetik kauçuk türlerinin arasında, SBR, tüketimi en fazla olan kauçukların başında gelmektedir.

Yaygın olarak kullanılan kauçuklar genellikle çok çeşitli katkı ve dolgu malzemeleri ile birlikte hamur halinde karıştırılarak üretilmekte ve bu malzemeler sayesinde özelliklerinde istenilen değişiklikler yapılabilmektedir. Dolgu maddelerinin kauçuk hamuruna katılmasıyla maliyet düşürülmekte ve/veya katkı malzemeleri kullanılarak işlenebilirlik, mekanik özellikler, fiziksel özellikler istenildiği gibi geliştirilebilmektedir.

Derinin yapısına bakıldığında üç boyutlu olarak çapraz bağlanmış kollajen lifler, keratin ve yağ gibi yapılara rastlanmaktadır. Derinin sahip olduğu kollajen yapı, biyolojik ve kimyasal bozunmasını önlemek amacıyla yapılan kromla tabaklama işlemleriyle kararlı hale getirilmektedir. Bu işlem sonucunda derinin fiziksel ve kimyasal özellikleri güçlenmekte ve görünüşünde de iyileşme meydana gelmektedir.

Üretim sırasında ortaya çıkan kromlu deri atıklarının (CTL) çevreye olan olumsuz etkilerinden dolayı, bu atıkların çeşitli yöntemlerle değerlendirilmesi gerekmektedir. Yapısında bulunan çapraz bağlı kollajen lifler sayesinde temel fiziksel özelliklerinin benzerlik gösterdiği kauçuk esaslı malzemelere katkı olarak kullanılmasının, bu atıkların değerlendirilmesi açısından iyi bir seçenek olduğu düşünülmüştür.

Bu çalışmada, CTL parçacıkları, NR, SBR ve NR/SBR kauçuk karışımlarına katılarak; ısıl ve morfolojik özelliklerdeki değişikliklerle birlikte, yaşlandırma öncesi

ve yaşlandırma (70 ^{o}C, 70 saat) sonrası mekanik özelliklerdeki değişimler de incelendi. CTL talaşları kauçuk karışımlarına eklenmeden önce yapısındaki nemi uzaklaştırmak amacıyla 80 ^{o}C`de 6 saat etüvde bekletildi. Elek analizi sonuçlarında kullanılan CTL katkısının %77,6 oranındaki kısmının boyutlarının 500-2000 μm arasında değiştiği kaydedildi. CTL katkısının NR, SBR, NR/SBR kauçuk karışımlarına etkisinin incelenmesi için farklı oranlarda karışımlar hazırlandı. Bu oranlar her kauçuk türü için bir adet deri katkısı içermeyen referans numune olmak üzere 5, 10, 15 ve 20 phr CTL içerecek şekilde belirlendi. Bütün bileşenler laboratuvar tipi dahili karıştırıcıda (banbury) yaklaşık 10 dakika süren karışım işlemiyle kademeli olarak karıştırıldı, sonrasında hem homojenizasyonu sağlamak hem de plaka haline getirmek için açık milden geçirildi. Diferansiyel taramalı kalorimetre (DSC) ile yapılan analiz sonucunda karışımların kürleşme pik entalpileri (ΔH_c) elde edildi. NR ve %1`lik amonyak solüsyonu ile nötralize edilmiş CTL katkısının bulunduğu NRN karışımlarında deri katkısının ΔH_c değerlerinin arttırdığı ancak SBR ve NR/SBR karışımlarında ise ΔH_c değerlerini azalttığı görüldü. Karışımların kürleşme davranışları 160 ^{o}C sıcaklıkta reometre cihazı (MDR) ile belirlendi. Minimum tork (M_L), maksimum tork (M_H), ön pişme süresi (t_{s2}), M_H-M_L aralığındaki tork değerinin %90`ını elde edebilmek için gerekli olan süreyi ifade eden optimum pişme süresi (t_{90}) gibi reometre parametreleri elde edildi. Artan deri katkısının kauçukların pişme sürelerini azalttığı görüldü. NR ve NRN karışımları için pişme süresinin 1,5 ile 2 dakika, SBR karışımları için 2 ile 5 dakika, NR/SBR karışımları için 2 ile 3 dakika arasında değiştiği gözlemlendi. Vulkanize edilecek kauçukların kalıp için gerekli miktarının tayin edilebilmesi için yoğunluk ölçme cihazından faydalanıldı. Vulkanizasyon işlemi, DSC ve reometre sonuçlarından elde edilen verilere göre 160 ^{o}C`de 140 bar basınçta hidrolik preste gerçekleştirildi. Numuneler 2 mm ve 6 mm kalınlıklardaki plakalar halinde hazırlandı. Örnekler, standart kalıplar kullanılarak çekme testi için papyon ve yırtılma testi için pantolon şeklinde kesildi. Kopma dayanımı, kopmadaki uzama, yırtılma dayanımı gibi değerler genel amaçlı çekme cihazı kullanılarak elde edildi. Deri katkısının NR ve NRN kompozitlerinin kopmada uzama, kopma dayanımı ve yırtılma dayanımı değerlerini bir miktar etkilediği ancak SBR ve NR/SBR kompozitlerinde bu değerlerde iyileşme sağladığı görüldü. Sertlik değerleri Shore A sertlik ölçüm cihazıyla belirlendi. Kompozitlerin aşınma dirençleri, yük altında kalıcı deformasyon davranışları da ölçüldü. Yük altında kalıcı deformasyon değerlerini belirlemek için örnekler kalınlıklarının % 25`i oranında sıkıştırılarak oda sıcaklığında 22 saat bekletildi.

Değişik miktarlarda deri içeren kauçuk karışımlarının kütlelerinde bozunmayla meydana gelen değişiklikleri belirlemek amacıyla ısıl ağırlık ölçümü (TGA) cihazı kullanıldı. Artan deri katkısının karışımların bozunma sıcaklıklarını öne çektiği ve 400 ^{o}C sonrasındaki kalıntı miktarını azalttığı gözlendi.

Numuneler 70 ^{o}C ve 70 saat ısıl yaşlandırmaya tabi tutuldu ve yaşlandırma sonrası mekanik özelliklerdeki değişimler incelendi. Yapılan testlerde CTL miktarındaki artışın NR esaslı karışımların yaşlanma sonrası kalıcı deformasyon değerlerini kabul edilebilir bir miktarda arttırırken, SBR ve NR/SBR esaslı karışımların yaşlanma sonrası kalıcı deformasyon değerlerinde önemli artışlara sebep olduğu görüldü. Sertlik testi sonuçları değerlendirildiğinde CTL katkısının karışımların yaşlanma sonrası sertlik değişimine etki etmediği görüldü. Yırtılma testi sonuçlarından elde edilen veriler değerlendirildiğinde ise deri katkısının NR esaslı kauçuk karışımlarının yaşlanma sonrası yırtılma dayanımlarını etkilemediği, ancak SBR esaslı

kompozitlerin yaşlanma sonrası yırtılma dayanımlarının artışında, CTL miktarının artmasıyla birlikte bir azalışın meydana geldiği kaydedildi. NR/SBR esaslı karışımlarda ise bu azalma miktarının daha az miktarda olduğu görüldü. NR esaslı kompozitlerin yaşlanma öncesi çekme dayanımları artan CTL içeriğiyle paralel olarak azalırken yaşlanma sonrası çekme dayanımlarının deri katkısıyla birlikte arttığı kaydedildi. SBR esaslı kompozitlerde ise CTL katkısı yaşlanma öncesi çekme dayanımını değiştirmemesine karşın yaşlanma sonrası çekme dayanımlarında bir miktar düşüşe neden oldu. NR/SBR esaslı kompozitlerde ise yaşlanma öncesi çekme dayanımları CTL katkısından etkilenmediği gibi yaşlanma sonrasında da çekme dayanımlarında belirgin bir değişim gözlenmedi. Kopma uzaması sonuçlarında ise NR esaslı kompozitlerin yaşlanma sonrası değerlerinde CTL katkısının yaşlanma direncini arttırması sonucu, artan deri içeriğiyle birlikte artış meydana geldi. SBR–CTL kompozitlerinde ise artan CTL katkısının yaşlanma sonrası kopma uzama değerlerinde azalmaya neden olduğu kaydedildi. NR/SBR-CTL kompozitlerinde de farklı bir durum olarak CTL katkısının yaşlanma sonrası kopma uzama değerlerinde belirgin bir farklılaşmaya neden olmadığı belirlendi.

Nötralizasyon işleminin malzemelerin yaşlanma karakteristiklerine olan etkilerinin gözlenmesi amacıyla NR-CTL ve NRN-CTL kompozitleri seçildi ve baskı altında kalıcı deformasyon, sertlik, yırtılma dayanımı, çekme dayanımı ve kopmada uzama değerlerindeki değişimler incelendi. Nötralizasyon işleminin malzemenin yaşlanma sonrası kalıcı deformasyon değerlerini değiştirmediği gözlendi. Benzer şekilde sertlik değerlerindeki ve yırtılma dayanımlarındaki değişime de etki etmediği belirlendi. Bununla birlikte NR-CTL karışımlarında yaşlanma sonrası çekme dayanımları artan CTL miktarı ile artmasına karşın nötralizasyon işlemi sonrasında yapılan yaşlandırma işleminde bu etki ortadan kalktı. Aynı şekilde yaşlandırma sonrası kopmada uzama değerleri nötralize edilmemiş deri katkısıyla artarken, nötralize edilmiş deri katkısında ise bu artış görülmedi.

1. INTRODUCTION

Elasticity is measure of tendency of solid materials to return to their original shape after being forces are applied on them. Perfectly elastic materials return to their original shape and size when the forces are removed, and the elasticity of these kinds of materials is 100%.

Some polymers can exhibit high elastic behavior due to their structural properties. *Natural Rubber* (NR) is the one of these and first high elastic polymer people used. First synthetic rubber that produced as industrial is neoprene (Poly(chloroprene)). Depend on polymer chemistry, especially after 1950s, different synthetic rubbers were improved and brought into use. Due to outstanding properties, natural rubber saves the value even nowadays.

Although "*rubber*" naming is for NR, after synthetic rubbers had improved, it has been using for all polymers that elongate reversible. Polymers that have rubber-like properties are also called "*elastomers*".

Unvulcanized (uncrosslinked) rubbers are sticky, nondurable against to chemicals and materials that have poor mechanical properties. After vulcanization, rubbers exhibit good performance due to their crosslinks. However, even some crosslinked rubber types do not have enough resistance to thermal aging in the presence of oxygen; it is necessary to compound with required ingredients.

NR involves 40% of total rubber consumption. The most widely using synthetic rubber is *Styrene-Butadiene Rubber* (SBR). SBR involves 40% of total rubber consumption (Lembaga Getah Malaysia, 2015). *Butyl Rubber* (IIR), *Acrylonitrile-Butadiene Rubber* (NBR), *Poly(chloroprene)* (CR) are other important rubbers.

Desired properties are given to rubbers by crosslinking and additives. Various additives are used such as carbon black (CB), calcium carbonate, silica, talc, and calcite. Also powdered leather wastes may also be utilized as additive.

Leather has three-dimensional crosslinked structure and that is actual natural polymer; tanning process is also necessary to improve its biological, chemical, physical and apperance properties (El-Sabbagh S. H. and Mohamed O. A., 2011). Tanning process is especially important for providing biologically stability (against bacterial attacks) to skin matrix. Tanning is essential for the reaction of collagen fibers in the hide with tannings, chromium, alum, or other chemical agents. The most common tanning agents are trivalent chromium and vegetable tannins extracted from specific tree barks. Chrome-tanned leather tends to be softer and more pliable than vegetable-tanned leather, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable-tanned leather. The first step of the process -soaking, fleshing, liming, deliming, bating and pickling- and the drying or finishing step are the same as in vegetable tanning. However, in chrome tanning, the additional processes of retanning, dyeing, and fatliquoring are usually performed to produce usable leathers. (U.S. Environmental Protection Agency, 1995) Chromium(III) has been used widely in tanning for the excellent properties that is renders to the leather along with simplicity of operation (Ramasami T. and Sreeram K. J. 2003).

In this study, chrome tanned leather scraps were added into NR, SBR, NR/SBR 50/50 blend compounds in different compositions using banbury mixer and two roll mills. It has been studied that morphological, curing, thermal, and mechanical changings of rubber compounds with different CTL contents. Curing properties of uncured rubber compounds were obtained by moving die rheometer (MDR) and curing peak enthalpies were attained using differential scanning calorimeter (DSC). Thermal gravimetric analysis (TGA) was used to investigate mass loss of sample by applying heat.

The samples were vulcanizated in hot press at 160 ^{o}C measured time by MDR.

Universal testing machine was used to obtain mechanical properties of rubber compounds such as elastic modulus, tensile strength, elongation at break, tear strength. Abrasion resistances of samples were obtained using rotary drum abrader. Hardness values of samples were measured by durometer. Crosslink densities were calculated by swelling method. All samples have been aged at 70 ^{o}C for 70 hours. To study aging effects on mechanical properties, same mechanical tests are applied aged samples.

2. THEORETICAL PART

Rubbers are polymers that can be vulcanized, in other words they are uncrosslinked but have the ability of crosslinking. Rubbers are classified as elastomeric materials. Generally, elastomers have been used in many industries. Elastomers (natural and synthetic rubber) are amorphous polymers and mostly cannot be used alone, some ingredients can be added and it is called “compound”. After vulcanization reaction, these materials become “rubber”. While they are elastic, they also dissipate applied energy because of their viscoelastic nature. As compared to other plastic materials, rubber materials behave more elastic, especially under shear and compressive deformations (Hertz and Gent, 2012).

2.1 History of Rubber

Europeans had met rubber first time when Christopher Columbus` second voyage to America in between 1493-1496. In 19th century, three important events had changed natural rubber history and laid the foundations of development process of rubber industry. In 1820, English Thomas Hancock had invented the mastication of rubber, therefore, incorporation of fillers into rubber easily and modelling had been realized by softening rubber. In 1823, Mackintosh had used some methods to produce waterproof clothes. Although all these developments, rubber could not had been used commonly due to softening under sun and hardening under cold. This problem had been solved thanks to Charles Goodyear`s invention of vulcanization in 1839. After Goodyear had invented that rubber can be crosslinked by sulphur, a great deal of industrial products that were suitable for the purpose produced (Morawetz, 2000). The major development of synthetic rubbers was seen in 1930s. When The World War II, Japan`s invading South-East Asia pushed Germany, America and their allieds which meet with difficulties for supplying of natural rubber to investigate synthetic rubber. In 1948, butadiene and styrene could have been copolymerized at +5 ^{o}C, -10 ^{o}C and even lower temperatures (Vahapoğlu, 2006; Long, 2001).

2.2 Types of Rubber

2.2.1 Natural rubber (NR)

Natural rubber (see Figure 2.1) is produced from the latex of Hevea Brasiliensis tree. Latex is an aqueous colloid of NR, and is obtained from the tree by "tapping" into inner bark and collecting the latex cups. The latex typically contains 30-40% dry rubber by weight, and 10-20% of the collected latex is concentrated by creaming, or centrifuging, and used in its latex form (Simpson, 2002)

NR is a natural polymer composed of an association of poly (cis-1,4-isoprene) [poly(2-methyl-1,3-butadiene)], of molecular weight 200,000-500,000, and biological elements, giving it highly specific properties (Höfer R., 2009).

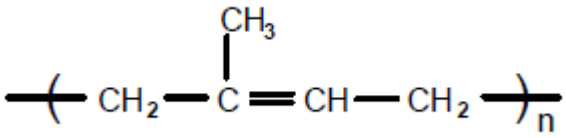


Figure 2.1: Chemical structure of NR

Each isoprene unit has a double bond. These double bonds provide crosslinking with sulphur and peroxides for natural rubber but also cause lowering resistance against ozone and oxygen. NRs can be vulcanized by a couple of systems such as sulphur, sulphur donating systems, peroxides. Service temperature is changed between -60 ^{o}C and 90 ^{o}C. Natural rubber shows high performance even at low temperatures due to fact that the glass transition temperature (T_g) is around -70 ^{o}C (Simpson, 2002).

Natural rubber has very unique mechanical properties such as high tensile strength, high elongation at break, low permanent deformation. However, resistance of NR against to heat, ozone, oils and hydrocarbons is low.

2.2.2 Synthetic rubbers

2.2.2.1 Styrene-butadiene rubber (SBR)

When the USA and Germany were cut off from the supplies of natural rubber during the Second World War both countries sought to produce a synthetic alternative; SBR was the result, and at one stage it was the most commonly used synthetic rubber. SBR (see Figure 2.2) is a synthetic copolymer composed of styrene and butadiene. It

can be produced by both emulsion and solution polymerization techniques. Both random emulsion and solution polymerized SBR contain about 23% styrene.

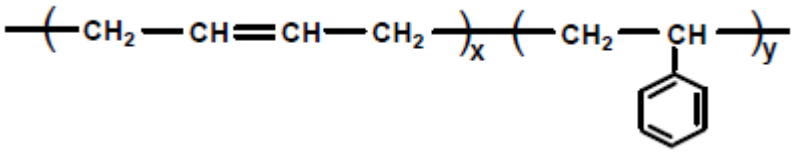


Figure 2.2: Chemical structure of SBR

SBR continues to be used in many of the applications where it earlier replaced natural rubber, even though it requires greater reinforcement to achieve acceptable tensile and tear strengths, and durability. However, the oil resistance of SBR is poor, and the polymer is not resistant to aromatic, aliphatic or halogenated solvents. Due to the unsaturation in the main chain, protection is required against oxygen, ozone and UV light.

Oil extended SBR, and SBR carbon black masterbatches are supplied by the polymer producers and such grades give the advantage of reducing the necessity of further additions of filler and oil at the mixing stage.

SBR can be cured by the use of sulphur, sulphur donor systems and peroxides. Sulphur cures generally require less sulphur (1.5-2.0 phr) and more accelerator than is normally required to cure natural rubber (Simpson, 2002).

2.2.2.2 Acrylonitrile-butadiene rubber (NBR)

Nitrile rubber (NBR) (see Figure 2.3) is a copolymer of acrylonitrile and butadiene. NBR is resistant against oils and solvents due to polar nitrile groups in polymer units. NBR is commonly considered the workhorse of the industrial and automotive rubber products industries. NBR is actually a complex family of unsaturated copolymers of acrylonitrile and butadiene.

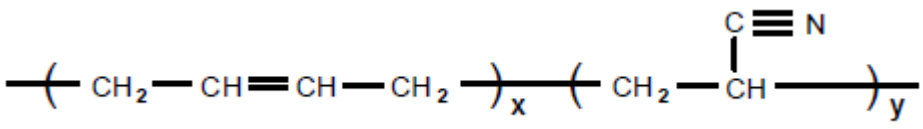


Figure 2.3: Chemical structure of NBR

By selecting an elastomer with the appropriate acrylonitrile content in balance with other properties, the rubber compounder can use NBR in a wide variety of

application areas requiring oil, fuel, and chemical resistance. In the automotive area, NBR is used in fuel and oil handling hose, seals and grommets, and water handling applications.

2.2.2.3 Butadiene rubber (BR)

Butadiene rubber is also known as polybutadiene (see Figure 2.4) (BR). Polybutadiene is produced by solution polymerization, and one important feature governing the performance of the resultant polymer is the *cis* 1,4, and 1, 2 vinyl contents. High *cis* 1,4 polymers (>90%) have a T_g around –90 °C, and hence exhibit excellent low temperature flexibility only exceeded by the phenyl silicones. They also exhibit excellent resilience and abrasion resistance; unfortunately the high resilience gives poor wet grip in tire treads, and hence this rubber finds limited use as the sole base for such compounds.

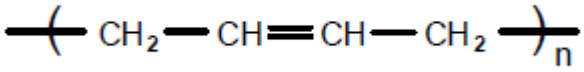


Figure 2.4: Chemical structure of BR

Peroxides, sulphur or sulphur donor system can be used to cure polybutadiene based compounds. Less sulphur and a higher level of accelerators are required when compared to NR.

Most polybutadiene is used in tire applications, and the majority of this use is in blends with other polymers, such as NR and SBR, where polybutadiene reduces heat build-up and improves the abrasion resistance of the blend. The friction on ice of winter tires is also improved by using higher levels of polybutadiene in the tread blend (Simpson, 2002).

2.2.2.4 Ethylene-propylene rubber (EPM/EPDM)

Copolymerization of ethylene and propylene produces an elastomeric polymer that is virtually inert because of the absence of carbon-carbon double bonds (EPM). Such polymers thus tend to be crosslinked with peroxides or by radiation (see Figure 2.5).

To improve the reactivity of ethylene-propylene copolymers, 1–10% of a third monomer can be added to give a terpolymer or ethylene-propylenediene monomer (EPDM). The primary diene monomers used in EPDM are 1,4- hexadiene, dicyclopentadiene, and ethylidene norbornene. Introduction of an unsaturated

monomer such as ethylidene norbornene will enable use of sulfur-based crosslinking systems.

EPDM tends to show good resistance to ozone attack, oxidation resistance, and moisture resistance. It is therefore used in applications that require good weather resistance and heat stability (Rodgers and Waddell, 2013).

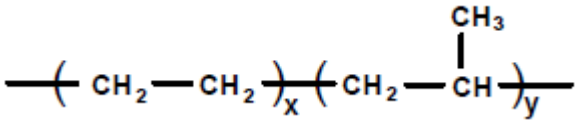


Figure 2.5: Chemical structure of EPM

EPM and EPDM are not oil resistant, and are swollen by aliphatic and aromatic hydrocarbons, and halogenated solvents. They have excellent electrical properties and stability to radiation. Their densities are the lowest of the synthetics, and they are capable of accepting large quantities of filler and oil (Simpson, 2002).

2.2.2.5 Butyl rubber (IIR)

Isobutylene (see Figure 2.6) is another useful monomer for rubber production and "polyisobutylene (PIB)" or "butyl rubber" is obtained by polymerization of isobutylene. Two major properties of polyisobutylene are low gas permeability and high energy absorption. Polyisobutylene cannot be crosslinked by conventional methods due to not including double bond on polymer chain. Therefore, polymer that is suitable for vulcanization is obtained by copolymerization with 0.5-3% isoprene. Naming "butyl rubber" is not used for homo-polymer polyisobutylene (PIB) but for isobutylene-isoprene copolymer and it is indicated by IIR abbreviation.

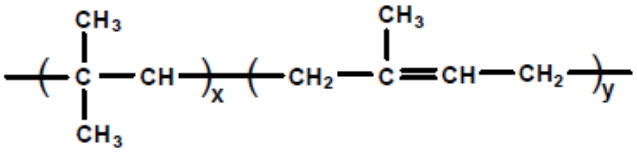


Figure 2.6: Chemical structure of IIR

IIR has some properties similar to those of EPDM, such as good mineral acid and base resistance and weather resistance which is similar to that of EPDM. IIR has excellent resistance to permeability by gases.

Applications include mounts and bumpers for vibration and shock prevention, roof and tank linings, curing bladders and inner tubes for tires. A significant use is inner

liners for tubeless tires, where halobutyl is preferred due to improved interplay adhesion with the rest of the inner tire. Halobutyl is also known as halogenated butyl rubber. This term is used for the rubber that includes halogene such as flour, bromine, chlor. Halobutyls can be blended with unsaturated elastomers such as NR, whereas for IIR it is not recommended.

2.2.2.6 Neoprene rubber (CR)

Polychloroprene (see Figure 2.7) that is produced by polymerization of chloroprene (2-chloro-1,3-butadiene) is first synthetic rubber which is also known as neoprene. Since it is not possible to commercially produce a polymer that is based on the *cis* 1,4 form, commercial polymers are based on the *trans* 1,4 form.

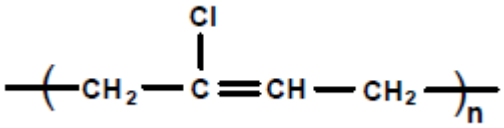


Figure 2.7: Chemical structure of CR

Due to its balance of strength, oil resistance, inflammability, increased resistance to ozone, ageing and weathering, polychloroprene finds widespread industrial use. Typical uses are V-belts, conveyor belts, wire and cable jacketing, footwear, wet suit applications, coated fabrics, inflatables, hoses, extrusions and many other goods. Adhesives are also a strong market area for CR (Simpson, 2002).

2.2.2.7 Synthetic isoprene rubber (IR)

This synthetic rubber (see Figure 2.8) has the same empirical formula as NR and hence closely approximates to the behavior of its naturally occurring rival. It has the same *cis* structure as NR, good uncured tack, high gum tensile strength, high resilience and good hot tear strength.

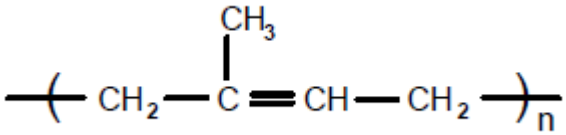


Figure 2.8: Chemical structure of IR

Although similar to NR it does exhibit some differences:

- It is more uniform and lighter in color than NR.
- Due to a narrower molecular weight distribution it exhibits less of a tendency to strain crystallize, hence green strength is inferior, as are both tensile and tear strength.

In general synthetic IR behaves like NR during processing, and it also requires protection against oxygen, ozone and light due to unsaturation in the main chain. Oil resistance is poor and it is not resistant to aromatic, aliphatic and halogenated hydrocarbons. It is resistant to many inorganic chemicals, but not to oxidizing acids and has limited resistance to mineral acids. It is unsuitable for use with organic liquids in general, the major exception being alcohols of low molecular weight (Simpson, 2002).

2.2.2.8 Silicon rubber (Q)

Unlike the previously discussed elastomers, which have carbon-carbon backbones, silicone rubbers contain very flexible siloxane backbones and have very low glass transition temperatures. The most common silicone elastomer is poly(dimethyl siloxane) with a T_g of -127 ºC. Silicone rubbers (see Figure 2.9) have both excellent high temperature resistance and low temperature flexibility. In addition, they possess good biocompatibility and thus are used in implants and prostheses. Other uses include gaskets, seals, and O-rings (Ciullo and Hewitt, 1999).

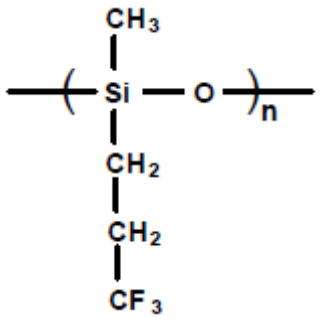


Figure 2.9: Chemical structure of Q

2.3 Basic Rubber Ingredients

Rubbers materials are mixture of some ingredients and raw gum elastomers. This mixture called rubber compound. Adding ingredients can be antioxidants,

accelerators, crosslinking agents, UV stabilizators. These materials effect on not only end-use product properties but also processing behavior of compounds. A typically rubber compound would likely contain at least the materials listed in Table 2.1. (Sommer, 2009).

Table 2.1: Basic rubber components.

Materials	Function
Elastomer or blend of elastomer	Provide rubbery behavior to the compound
Fillers	Modify modulus and processing properties
Protective agents	Protect compound from oxygen and ozone
Vulcanization additives	Crosslink elastomer chains

An example formulation for rubber compounds is given in Table 2.2 (Ferreira et al, 2011).

Table 2.2: A sample receipt.

Components	Example	phr
Raw rubber	SBR-NBR	100
Filler	Silica	30
Activators	PEG, Stearic Acid, Zinc carbonate	6
Antioxidant	Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	3.5
Accelerator	MBTS, TMTD	1.5
Vulcanization agent	Sulfur	1.5

2.3.1 Raw gum elastomer

Raw gum elastomer (base polymer) is the main ingredient and can consist of natural or synthetic rubber, or thermoplastic elastomers. These elastomeric materials have important role on the properties of final products. It is therefore always at the top of the formulation list and is expressed as 100 parts by weight of the total recipe.

It is accepted convention in the rubber and plastic industries to base all ingredients as "parts per hundred resin/raw rubber" or "phr." This means that the total parts of one, two, three, or more different rubbers called for in a specific recipe must be defined as

100. Thus, all the other non-rubber ingredients are rationed against this "100 parts" (that represents all rubber hydrocarbon). (Hewitt N., 2007)

2.3.2 Fillers

While the vulcanizated raw gum elastomers of NR and CR are mechanically strong, most gums are weak when vulcanizated and they need reinforcing fillers. As the term implies, there is a reinforcement effect, the empirical results of which are to increase mechanical strength (for example tensile strength and resistance to tearing) in the vulcanizate, and to increase stiffness. Addition of filler effects hardness of the cured product. All fillers are not created equal, so that there is a range of reinforcement from very high to very low, corresponding to the primary size of the filler particle, from around 10 nm for very fine particle carbon blacks giving high reinforcement, to greater than 300 nm for some calcium carbonates which give low reinforcement. Use of the latter reduces compound cost. The shape and surface chemistry of the filler particle also play an important part in reinforcement. Some popular fillers are carbon blacks, silicas, clays and whitings (calcium carbonate, also known as chalk). (Ciesielski, 1999)

2.3.2.1 Carbon black

Carbon black (CB) is has been widely used to produce many types of rubber products, because CB functions as a filler to reinforce various mechanical properties such as modulus, tear strength and wear characteristics of products. It is well known that the reinforcing effect of CB is mainly due to strong interactions between the polymer and the CB surface (Wolff and Wang, 1993; Leblanc, 2002). Because of such strong interaction, when rubber polymer and CB filler are mixed, some polymer becomes insoluble even in a good solvent.

There are several ways of manufacturing of CB. Subsequently, natural gas was used as a source for what is called the “channel black” process. This method burns natural gas at about 1300 °C and collects carbon black deposited on steel channels. When exposed to air at high temperature, channel process carbon blacks appear to become porous.

In the acetylene black process, acetylene is burned with air depleted of oxygen. This gives pure carbon blacks, but of large particle size.

The “oil furnace” process involves a liquid hydrocarbon, usually a heavy petroleum oil, which is injected, sprayed, and mixed with preheated air and natural gas in a reactor. Part of the hydrocarbon is burned to maintain the reaction temperature ranges of 1450 to 1800 °C and the remainder is converted to carbon black. This process has a lower residence time and yields a narrower distribution of carbon black aggregate sizes, higher surface activity, and open aggregates (branched or grapelike/bulky).

Today, carbon black is produced commercially by the above oil furnace procedure, the incomplete combustion of refinery heavy bottom oils. These carbon blacks are referred to as “furnace blacks”, as opposed to earlier carbon blacks that, as described above, were produced from natural gas and are called “channel blacks” (Hofmann, 1989; Donnet and Vogt, 1976; Byers, 1987). Some carbon black types, particle sizes according to ASTM and BET results that measured as a function of relative pressure using a fully automated analyzer of given CB code are shown in Table 2.3.

Table 2.3: Some CB types and their properties.

ASTM N-type	ASTM Particle Size (nm)	Code	BET (m^2/g)
N100 to N199	11-19	N110	145
N300 to N399	26-30	N330	82
N500 to N599	40-48	N550	43
N700 to N799	61-100	N762	28
N900 to N999	201-500	N990	7-12

2.3.2.2 Silica

Silica is compounded into thermoplastics, thermosets, and elastomers. The commercial silica used in the polymer industry is amorphous. Synthetic silicas are manufactured by various methods; fumed, electric arc, fused, gel, and precipitated. Vapor or pyrogenic process produces fumed and electric arc silicas. Fusing a high-purity quartz at high temperature produces fused or vitreous silica. Hydrated silica is produced by a liquid or wet process. All synthetic silicas are amorphous in nature, have a chemical composition of SiO_2, and are colorless, odorless, tasteless, fine-particle white powders. Silicas are chemically inert and insoluble powder. They are,

however, soluble in strong alkali (NaOH) and hydrofluoric acid (HF) (White and Kim, 1962). Silica is used as reinforcing filler in rubber industry.

2.3.3 Activators

Realization of the full potential of most organic accelerators and cure systems requires the use of inorganic and organic activators. Zinc oxide is the most important inorganic activator, but other metallic oxides (particularly magnesium oxide and lead oxide) are also used. Although zinc has long been termed an activator, zinc or another divalent metal ion should be considered to be an integral and required part of the cure system. The most important organic activators are fatty acids, although weak amines, guanidines, ureas, thioureas, amides, polyalcohols, and amino alcohols are also used.

The large preponderance of rubber compounds today use a combination of zinc oxide and stearic acid as the activating system. Several studies (Barton and Hart, 1952; Adams and Johnson, 1953; Trivette et al., 1962) have been published on the effects of variations in the concentrations of these activators. In general the use of the activators zinc oxide and stearic acid improves the rate and efficiency of accelerated sulfur and peroxide vulcanization (Hoover and To, 2004) Zinc oxide (ZnO)

Zinc oxide, Chinese white, or zinc white, is prepared; 1- by oxidizing pure zinc metal, and 2- by roasting zinc oxide ore (Franklinite) with coal and subsequent air oxidation. The particle size of commercial zinc oxides usually ranges from 0.1 to 0.4 μm, and its BET area ranges from 10 to 20 m^2/g. Particles having an average size of 0.036 μm (36 nm) have been produced with a higher BET area at 15 to 45 m^2/g with little porosity (Tanaka et al., 1997).

Zinc oxide is a crystalline, odorless, and white or yellowish white powder. It absorbs carbon dioxide from the air, has high UV absorption, and is used as an antiseptic additive. It is insoluble in water and alcohol but soluble in acid, ammonium carbonate and alkali hydroxide solutions. Zinc oxide is used as a filler and accelerator-activator in rubber and plastics.

In the early rubber industry, zinc oxide was the particle reinforcement of choice. In first years of the 20^{th} century it was replaced by carbon black. Compounds with carbon black had higher particle loading and smaller particles than zinc oxide and

gave superior mechanical properties and were more processable. Today small amounts are retained in rubber compounds for their ability to enhance vulcanization/crosslinking processes involving sulfur (White and Kim, 1962).

2.3.3.3 Stearic acid

Stearic acid is often used in the rubber industry in carbon black compounds as a vulcanization activator (Turner and Moore, 1980). When a carboxylic acid is mixed into a rubber compound, it melts and is rapidly incorporated into the compound but usually does not dissolve. This depends on the type of rubber. If stearic acid is insoluble, it can act as a processing aid.

These two materials, together with sulfur and accelerator, constitute the 'cure system' for the formulation. Zinc oxide reacts with stearic acid to form zinc stearate (in some cases zinc stearate is used in place of zinc oxide and stearic acid) and together with the accelerator they speed up the rate at which sulfur vulcanization occurs. With sulfur alone, the curing process might take hours. Using this curing system, it can be reduced to minutes.

2.3.4 Antioxidants

Ozone attack occurs mainly at the olefinic double bond of an unsaturated (diene) rubber and, if not protected against, will results in loss of physical integrity for thin sectioned articles and surface cracking on thick sectioned products (Ullman, 1993; Elias, 2008).

There are two principal methods by which ozone attack can be prevented:

- Having an impermeable layer on the rubber surface
- Incorporating a chemical antiozonant to hinder the auto ozonation reaction.

The first method involves the addition of waxes (microcrystalline wax, paraffin wax, etc.) as a compounding ingredient, which in service will bloom on the rubber surface. This layer will act as physical barrier for the ozone to attack the unsaturation site. Two important properties are intended to be important in case of selection of waxes: rate of migration and melting point. Above the melting point of the wax, its protective action will nullify and the rate of migration determines the how fast the layer is forming. It is a common practice to use the blends of waxes to provide a

protection against wide range of temperature. In addition to that, most widely used antiozonants are the substituted *p*-phenylenediamines.

They not only offer protection against ozone but also function as antioxidants and as outstanding antiflex agents. One major drawback is that they are discoloring and staining. They can be conveniently grouped into three categories based on the chemical nature of substituents: diaryl-*p*-phenylenediamines (DAPD), dialkyl *p*-pheylenediamines (77PD) and alkyl-aryl-*p*-phenylenediamines (IPPD, 6PPD).

The second method is the addition of chemical ingredients which will hinder the reaction path of ozonation. Benzofuran derivatives and enolethers are offered as chemical antiozonants for light coloured rubber compounds. Benzofuran derivatives are used in CR and its blends with other rubbers and give ageing protection in addition to ozone protection. The enolethers give ozone protection but not ageing protection with NR, IR, SBR, BR, but are less effective in NBR (Shanks and Kong, 2013).

2.3.4.1 *N*-2-Propyl-*N'*-phenyl-*p*-phenylenediamine (IPPD)

N-2-Propyl-*N'*-phenyl-*p*-phenylenediamine (IPPD) is used as an antioxidant and antiozonant for natural and synthetic elastomers and as an antiflex agent for the protection against catalytic degradation by copper and other heavy metals.

2.3.4.2 1,2-dihydro-2,2,4-trimethylquinoline (TMQ)

Amine antioxidants in general are better antioxidants than phenolic antioxidants. However, most amine antioxidants are discoloring and staining and have limited approval for food contact use. The materials can be categorised as: naphthylamines, diphenyl amine derivatives, dihydroquinolines and paraphenylenediamines. Most commonly used secondary amine is polymerized 1,2-dihydro-2,2,4-trimethylquinoline (TMQ) (Shanks and Kong, 2013).

2.3.4.3 Microcrystalline wax (MC Wax)

Wax types like microcrystalline wax (MC Wax) are used for improved weather resistance because they migrate to the outer surface of the compound, resulting in protection of the compound ingredients from leach out (White and Kim, 1962).

2.3.5 Accelerators

The accelerator (not to be confused with a catalyst, which remains fully available at the end of a chemical reaction), is usually understood to mean an organic chemical, and as the name implies, it speeds up the rate of vulcanization.

There are many accelerators available to the rubber chemist, grouped into several chemical classes. Some have a built in delay time, so that when heat is applied to the compound at the beginning of the curing process, no vulcanization (crosslinking) takes place for a specified initial period of time. They are appropriately called delayed action accelerators, an example would be the sulfonamides. This delay is highly beneficial if a compound takes a long time to completely fill a cavity in a heated mold. Sometimes, only a very short induction (delay) time is needed, and the dithiocarbamates provide this. Occasionally an accelerator with a slow rate of cure might be needed, such as the guanidines, or maybe a fast cure as given by the thiurams and dithiocarbamates.

Some accelerators are able to provide sulfur from their own chemical structure, so that the need for elemental sulfur might be reduced or eliminated in the formulation. They are called sulfur donors, and examples are tetramethylthiuram disulfide (TMTD), and dithiodimorpholine (DTDM). Sulfur donors provide monosulfidic crosslinks which impart improved compression set and heat resistance.

2.3.5.1 N-cyclohexyl-2-benzothiazol sulfonamide (CBS)

N-cyclohexyl-2-benzothiazol sulfonamide (CBS). Long scorch with medium to fast cure. It would be a good choice when mixing compounds containing reinforcing furnace blacks which generate more heat. The sulfonamide *N, N'*-dicyclohexyl-2-benzothiazyl sulfonamide (DCBS) gives longer scorch and slower curing. DCBS gives excellent adhesion when bonding brass coated steel to rubber, for example in tire production (Ciesielski, 1999).

2.3.5.2 Tetramethylthiuram disulfide (TMTD)

Tetramethylthiuram disulfide (TMTD) provides less scorch time than that of dithiocarbamates so TMTD causes fast curing. Also TMTD is less scorchy in the absence of sulfur. In this case its function would be that of a cross-linking agent rather than an accelerator (Ciesielski, 1999).

2.3.6 Vulcanization systems

2.3.6.1 Sulphur vulcanization

Sulfur was the original vulcanizing agent used by Charles Goodyear in 1839 and today is the most common vulcanizing agent used in the rubber industry. Sulfur in the presence of heat reacts with adjoining olefinic bonds in the polymeric backbone chains or pendent chains of two elastomeric molecules to form crosslinks between the molecular chains. However, the sulfur may combine in many ways to form the crosslink network of vulcanized rubber. Sulfur may be present as monosulfide, disulfide, and polysulfide linkages. It may also be present as pendent sulfide and pendent cyclic mono- and poly-sulfides.

The conventional cure systems feature a high sulfur level and low accelerator concentration, which forms a higher level of polysulfide crosslinks whose bonding energy is the lowest among crosslinks. Therefore conventional cure systems show poor heat and oxidation resistance, and a longer chain of polysulfide crosslinks would provide better flex fatigue properties with lower modulus.

The efficient or semi-efficient cure systems feature a higher level of accelerators and sulfur donors and a lower level of free sulfur. These systems form mono- or di-sulfide crosslinks whose bonding energies are much higher than that of polysulfide crosslinks. They show good heat stability and oxidation resistance. However, they are inferior in flex fatigue because they have a shorter chain of crosslinks, which would have a higher modulus. A higher modulus compound generates higher heat energy during flex fatigue test, which would lead to break crosslink for an early failure (Hoover and To, 2004).

2.3.6.2 Peroxide vulcanization

Peroxides are suitable for curing rubber but are not recommended for some elastomers such as IIR or CIIR. Peroxides can be used to cure many elastomers, since, unlike sulfur, they do not need unsaturated bonds in the polymer. Thus they may be used to cure ether-type polyurethanes, certain fluoro-elastomers, silicones, and all of saturated elastomers. Peroxides can also be used to crosslink CR.

Although not nearly as popular as sulfur, peroxides have a distinct place in rubber compounding, and are a major curative for silicone rubber. In the basic rubber

compound formulation, the zinc oxide, stearic acid, sulfur and accelerator can all be replaced by a single material, the peroxide. Some care must be taken in compound formulation, to avoid unwanted interaction with peroxide. This applies, for example to antioxidant selection. Contact with oxygen (air) should be avoided during vulcanization (such as in hot air ovens or autoclave curing). Some ingredients, which are not part of the cure system, which are common in sulfur systems can interact with the peroxide in peroxide cure systems and thus interfere with cure. Use of peroxides as curing agents can confer some advantages. First an improvement in the heat aging resistance of the vulcanizate, thus upper temperature limits can be pushed up a little or the lifetime extended. Compression set is also improved. On the other hand, tensile strength, tear strength, and fatigue (dynamic deformation such as constant flexing) life are reduced. A post cure (continued cure outside of the mold) is sometimes undertaken with peroxide cured vulcanizates, to complete the cure and remove unwanted byproducts.

The crosslink density of a peroxide cured compound can be increased by addition of chemicals called coagents, of which methacrylates are a good example. This results in a higher state of cure with improvements in properties such as compression set (Ciesielski, 1999).

2.3.6.3 Electron beam curing

It is possible to achieve some vulcanization of rubber with a beam of electrons. Although not widely used throughout the industry such a process has found a place in partially cross-linking components of tires, as an aid to tire production, using a radiation dosage of about four megarads. Much higher doses would be needed to fully vulcanize even thin rubber sections. Work has been carried out on the post curing of an SBR compound with electron beams, with claims of a significant improvement in resistance to ozone and crack initiation (Ciesielski, 1999).

2.3.6.4 Miscellaneous

Sulfur is the classical crosslinking agent for unsaturated elastomers such as NR, SBR, NBR, BR, and EPDM. In some cases, such as halogen containing elastomers, the preferred agent is a metal oxide. For example, CR is typically cured with a blend of the oxides of magnesium and zinc, which cure by removing some chlorine from

the polymer chain. CIIR may also be cured with zinc oxide. For both elastomers and organic chemicals are typically added to increase curing. Fluoro-elastomers and polyacrylates may be cured with certain amines, and alternatively with bisphenols. (Ciesielski, 1999).

2.4 Rubber Processing

In rubber industry, mixing is the foundation step upon which every further step is dependent on. Mixing is the most critical component of rubber processing.

The aim of mixing is to produce a product that has the ingredients dispersed and distributed sufficiently thoroughly that will process satisfactory in the next process, cure efficiently and give the required properties for the end application.

Mixing requires deciding the formulation, what equipment to use, and the time, speeds, pressures, temperatures. The aim should be to minimize the labor, energy and equipment cost per unit volume of product. Due to the partly elastic nature and very high viscosity of rubber, power intensive, sturdy machinery like mixing mills and internal mixers are necessary (Anıl, 2014).

2.4.1 Banbury mixer

Banbury mixer is a tangential type internal mixing machine, in which two slightly spiraled rotors revolve side by side towards each other within a chamber shaped like two short cylinders lying together with adjacent sides open. The chamber has a top opening called hopper, which can be closed by pneumatic means for inserting the material and a bottom gate, which can be hydraulically opened, to drop out the contents after mixing. An industrial type banbury mixer is given below Fig. 2.10.

Banbury is charged by raising the ram completely out of hopper and dropping in bales of rubber weighed up properly to fill the chamber. The ram is then lowered under pressure and the rubber forced and held in the chamber while it is needed and blended by the rotors. Breakdown of rubber is accomplished by shearing action between rotor blade tips and rotor walls and between rotor-rotor, with one rotor running slightly faster than the other to prevent sticking to the blades.

Figure 2.10: Banbury mixer

Banbury mixer combines rubber stock, carbon black and other chemical ingredients. Compounding and Banbury mixing create a homogeneous rubber material. Time, heat and raw material are factors utilized to engineer material composition. The ingredients are generally provided to the plant in pre-weighed packages or are prepared and weighed by Banbury operator from bulk quantities. Measured ingredients are placed onto a conveyer system, and the Banbury is charged to initiate the mixing process (Anıl, 2014).

2.4.2 Two-roll mill

Two-roll mill process is also known as “Open Mill Process”. In this technic, rubber compound is drawn though rolling mills. Due to friction between compound and surfaces of the mills and compression on compound, mixing occurs. During process, rubber forms into a sheet and is cut by manually then it is fed again until gets homogenized or for certain time period. By changing distance between mills,

different shear forces can be applied on compound. As this process can be operated after banbury process, it also is used singular. Since cutting is operated by manually, experience of operator is important for this technic. An industrial type two-roll mill is given in Fig. 2.11.

Figure 2.11: Two-roll mill

2.5 Leather

Leather is a natural polymer that has collagen and three-dimensional crosslinked structure. To improve biological, chemical, appearance and physical properties of leather, tanning process is applied. While this process, large amounts of organic and chemical pollutants are showed up as a byproduct. Wastes generated by the leather processing industries pose a major challenge to the environment, according to conservative estimates, about 600,000 tons per year of solid waste are generated worldwide by leather industry (El-Sabbagh and Mohamed, 2011).

2.5.1 Chemical composition of leather

Leather is the hide or skin of animals such as:

- cows and other bovine species
- goats and kids
- sheep and lambs - without their wool
- swine
- reptiles like snakes, crocodiles and lizards

The generally used cattle hides contain 65–70% water, 30–35% dry substance, 9% lipids and <1% ash. The dry substance is made from fibrous proteins collagen, keratin, elastin, and reticulin.

Collagen, the principal protein of the hide, is the material that is made into leather. The reactivity of the collagen toward tanning agents and the dyeability, as well as the strength, flexibility, and durability of the collagen when tanned, are all important to making leather a material of choice for utility and fashion (Thorstensen, 2000).

Keratin, a fibrous protein forming main structural constituent of leather, hair, wool, horn, hoof etc., is abundantly available as a by-product, slaughterhouse, tanning and fur processing industry. Depending on the age of the animal and season of the year, keratin may constitute 6–10% of the total protein (Bailey, 2011).

2.5.2 Chrome tanning process

Leather tanning is the process of converting raw hides or skins into leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer. The three types of hides and skins most often used in leather manufacture are from cattle, sheep, and pigs.

Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents used in the U. S. are trivalent chromium and vegetable tannins extracted from specific tree barks.

Although the title of this section is "leather tanning", the entire leather making process is considered here, not just the actual tanning step.

"Leather tanning" is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. Production of leather by both vegetable tanning and chrome tanning is described below. Fig. 2.12 presents a general flow diagram for the leather tanning and finishing process. Trimming, soaking, fleshing, and unhairing, the first steps of the process, are referred to as the beam house operations. Bating, pickling, tanning, wringing, and splitting are referred

to as tanyard processes. Finishing processes include conditioning, staking, dry milling, buffing, and spray finishing, and plating (Bienkiewicz, 1983; U.S. Environmental Protection Agency, 1982).

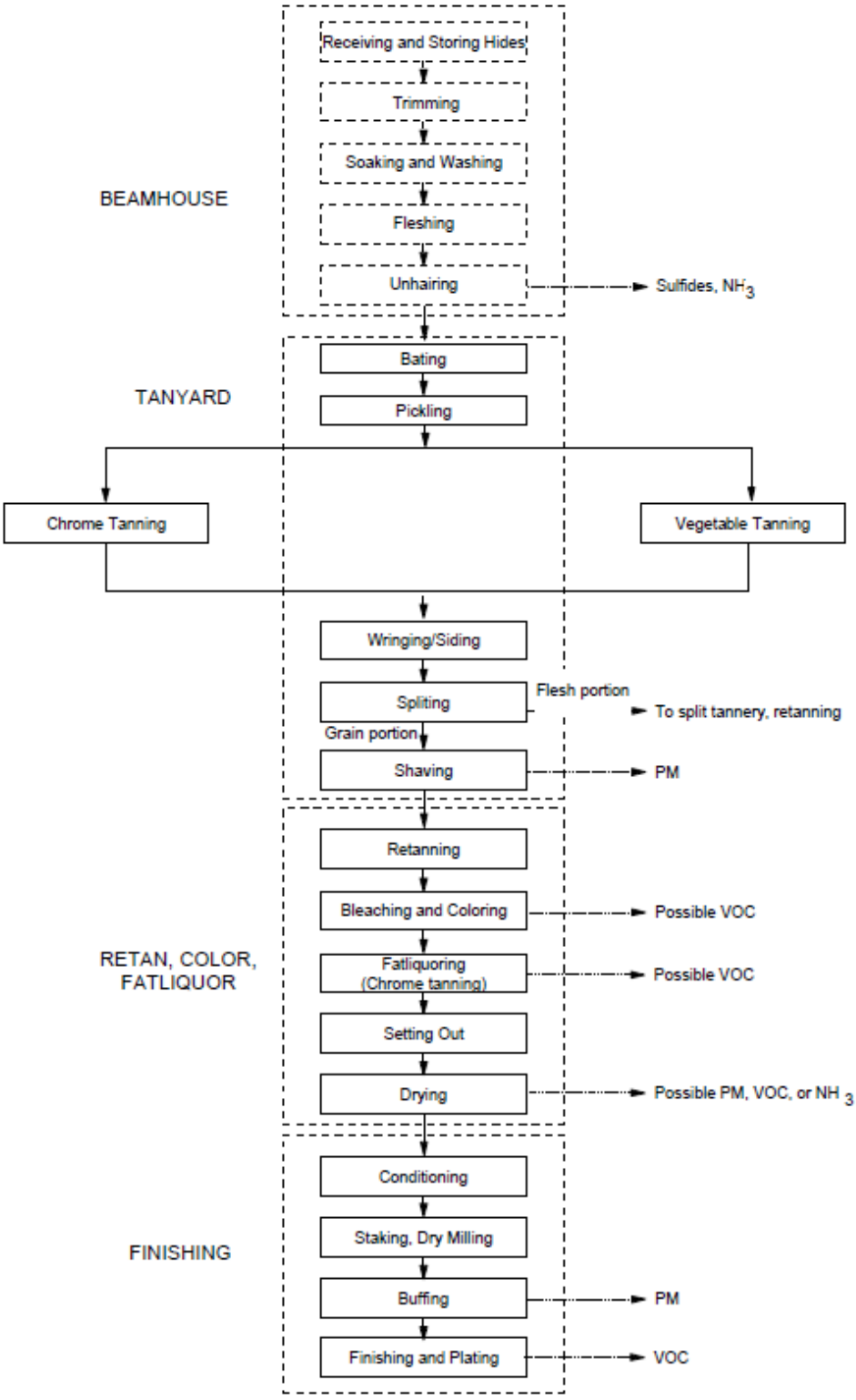


Figure 2.12: General flow diagram for the leather tanning and finishing process

2.5.3 Vegetable tanning process

Heavy leathers and sole leathers are produced by the vegetable tanning process, the oldest of any process in use in the leather tanning industry. The hides are first trimmed and soaked to remove salt and other solids and to restore moisture lost during curing. Following the soaking, the hides are fleshed to remove the excess tissue, to impart uniform thickness, and to remove muscles or fat adhering to the hide. Hides are then dehaired to ensure that the grain is clean and the hair follicles are free of hair roots. Liming is the most common method of hair removal, but thermal, oxidative, and chemical methods also exist. The normal procedure for liming is to use a series of pits or drums containing lime liquors (calcium hydroxide) and sharpening agents. Following liming, the hides are dehaired by scraping or by machine. Deliming is then performed to make the skins receptive to the vegetable tanning. Bating, an enzymatic action for the removal of unwanted hide components after liming, is performed to impart softness, stretch, and flexibility to the leather. Bating and deliming are usually performed together by placing the hides in an aqueous solution of an ammonium salt and proteolytic.

In the vegetable tanning process, the concentration of the tanning materials starts out low and is gradually increased as the tannage proceeds. It usually takes 3 weeks for the tanning material to penetrate to the center of the hide. The skins or hides are then wrung and may be cropped or split; heavy hides may be retanned and scrubbed. For sole leather, the hides are commonly dipped in vats or drums containing sodium bicarbonate or sulfuric acid for bleaching and removal of surface tannins. Materials such as lignosulfate, corn sugar, oils, and specialty chemicals may be added to the leather. The leather is then set out to smooth and dry and may then undergo further finishing steps. However, a high percentage of vegetable-tanned leathers do not undergo retanning, coloring, fatliquoring, or finishing.

2.6 Literature Review

The leather that is used in clothing is natural polymer including three dimension collagen crosslinked fibers, keratin and oil. The collagen structure of leather is rendered stable by tanning with chrome to prevent degradation. Unprocessed leather is bio-degradable but is tanned to render it suitable for use, therefore physical, chemical and biologic properties are improved (El-Sabbagh and Mohamed, 2011). Chrome salts and sodium chromate are commonly used in tanning process.

In production of leather wear during tanning process, waste that is composed by edge trimmings and called as “chrome shaving” comes out.

The chrome-tanned process generates huge quantities of solid waste and about 600,000 tons of chromium tanned wastes are produced annually worldwide of which 5-10% (w/w) are finished wastes and the rest is chrome shavings. (Covington et al., 2003; Afşar et al., 2006). Until recent date, mainly chrome shavings were adhesived by various binders such as latex in production of shoe insole and sideband also known as welt. Now, these products are made from polymer-based materials (e.g. polyurethane). Thereby, the amount of chrome shaving that should be removed and if it is possible it must be utilized in alternative usage areas increases day by day.

There are some recycling applications about leather-based wastes including chrome shaving by using as filler in polymeric material formulations. Andreopoulos et al. (2000) have incorporated leather wastes into PVC. The addition of the leather wastes caused that density and hardness of the composites increased. In the literature, limited numbers of studies are available related to utilizing of leather waste, especially chrome shavings, in rubber-based materials.

Most of rubbers cannot be processed without additives; fillers are used between 20%-100% in compounds of rubbers. Aliminium silicates, calcium carbonate, talc may be chosen to lower cost of rubber compounds (Saçak, 2005). Carbon black and silica increase processability of rubber, mechanical strength and lifetime by acting reinforcing material besides of filler properties.

These reinforcing materials used in rubber improve tear strength, abrasion strength and miscibility with other compound ingredients (Ansarifar et al., 2004). Increment in some mechanical properties and resistance to thermal aging of rubbers is observed when powder form of leather wastes added to rubber compounds (Chronska and Przepiorkowska, 2008; Przepiorkowska et al., 2007).

When waste leather fibers are added to elastomers, the former could function as short fiber reinforcement for the matrix provided the inherent fibrous nature of the former is retained during processing (CTC Report, 2000; Ravichandran and Natchimuthu, 2005a). Since processing of elastomers is carried out relatively at high temperatures, retention of the fibrous nature in leather under such conditions however is very difficult. However, since processing of elastomers is carried out at relatively high

temperatures, retention of the fibrous nature may be difficult. Additionally, use of leather in rubber formulations is prone to affect the vulcanization characteristics and vulcanizate properties due to the presence of reactive functional groups, trivalent chromium content, and its acidic nature (Ferreira et al., 2010). Therefore, leather wastes should be neutralized before adding to rubber. This step pushes up the cost of preparation of waste. It is confirmed that untreated leather scrapes change natural rubber vulcanization characteristics and cause lowering mechanical properties of vulcanizate due to acidic nature of leather (Ravichandran and Natchimuthu, 2005a, Ravichandran and Natchimuthu, 2005b).

Urea, ammonium, sodium carbonate or sodium formate solutions are commonly used during neutralization process (El-Sabbagh and Mohamed, 2011; Ferreira and Freitas, 2010; Ravichandran and Natchimuthu, 2005b). Chrome shavings treated with sodium carbonate and ammonium increase mechanical properties by effecting vulcanization characteristics (Natchimuthu et al., 1994). Adding chrome shavings to rubber increases tensile strength, elastic modulus and tear strength until a certain point, however elongation at break values are affected in acceptable tolerances (El-Sabbagh and Mohamed, 2011; Ferreira et al., 2010; Ferreira et al., 2011).

Chrome scraps (<0.2 mm) have been used as a filler for acrylonitrile-butadiene rubber and carboxylated acrylonitrile-butadiene rubber and obtained vulcanizates are reported with increased tensile strength, tensile strain and crosslink density (Chronska and Przepiorkowska, 2008; Przepiorkowska et al., 2007). Ferreira et al. (2011) used powder leather (<1.0 mm) in SBR and NBR based compounds and results have showed tear strength of the end product was increased (Ferreira et al., 2010, Ferreira et al., 2011). The effects of ammonium and sodium formate treated chrome shavings on mechanical properties of NBR/CTL compound were studied by El-Sabbagh and Mohamed (2011). Vulcanization process has increased tensile strength, tensile modulus at 100% elongation and hardness of vulcanizates. Also, they have reported swelling in toluene was reduced in other words crosslink density was increased (El-Sabbagh and Mohamed, 2011).

3. EXPERIMENTAL

3.1 Materials

3.1.1 Raw gum elastomers

3.1.1.1 Natural Rubber

NR, SIR20 was obtained from Elkim Kauçuk, Turkey. Plasticity retention index (PRI) is 60 and ash content is 0.4%.

3.1.1.2 Styrene-Butadiene Rubber

SBR, SBR 1502 was obtained from Elkim Kauçuk, Turkey. Volatile matter content is 0.33% and ash content is 0.26%.

3.1.2 Fillers

3.1.2.1 Chrome tanned leather scraps (CTL)

Chrome tanned leather scraps (shavings) were obtained from Kopuzlar Leather Company Co. Ltd, Tuzla Organized Leather Industry and then cut into smaller pieces. It has no Cr+6. Its moisture content is 45.71%.

Chrome tanned leather particles were used as untreated and treated by ammonium to neutralize. Neutralization process was performed using 1% ammonium solution. CTL particles were put to the solution for 72 hours at ambient temperature and then dried for two days.

3.1.2.2 Carbon black (CB)

Carbon Black, GPF N-660 with CTAB ADS of 35 m^2/g, density of 0.425 and pH=7 was obtained from Interplast, Turkey. It was used as filler.

3.1.3 Processing aids (aromatic oil)

Aromatic oil was kindly procured from Arsan Rubber Company, Turkey. Its viscosity at 100^{o}C, 65-82 Sayboult universal second (SSU) and its flash point is minimum 210 ^{o}C.

3.1.4 Activators

3.1.4.1 Zinc oxide

Zinc oxide with min 35.50% zinc was obtained from Hepşen Chemical Company Co.Ltd, Turkey. It was used for activator.

3.1.4.2 Stearic acid

Stearic acid was obtained from Kimpaz Chemical Company Co.Ltd, Turkey. It was used for activator.

3.1.5 Antioxidants

3.1.5.3 Microcrystalline wax

Microcrystalline wax (MC Wax) was obtained from Yılmaz Kimya Company Co. Ltd. It was used for antiozonate.

3.1.5.4 IPPD

Vulcanox 4010 NA/LG with 1.04 g/cm^3 density, 76 °C melting point and 0.1 % ash content was obtained from Lanxess Company Co.Ltd, Turkey. It was used as antioxidant.

3.1.5.5 TMQ

Vulcanox HS/LG with 1.04 g/cm^3 density, 90 °C softening point and below 0.3 % ash content was obtained from Lanxess Company Co.Ltd, Turkey. It was used as antioxidant.

3.1.6 Accelerators

3.1.6.1 CBS

CBS was obtained from Deltagran Company Co. Ltd. and used as accelerator.

3.1.6.2 TMTD

TMTD was obtained from Deltagran Company Co. Ltd and used as accelerator.

3.1.7 Sulphur

Sulfur, Rhenogran S-80 with 80% sulfur, 20% elastomer binder and dispersing agents was obtained from Lanxess Co.Ltd, Turkey. Its density is 1.64 g/cm^3 approximately. It was used as curing agent.

3.2 Equipments for Compounding

3.2.1 Sieve analyzer

Sieve analyzer (Figure 3.1) was used to determine of particle size distribution of CTL shavings using in Figure 3.2 below device. Different mesh sizes of pans were added up and it was sifted at 50 Amplitude during 10 minutes. Then weights were measured in the pans and separation was completed.

Figure 3.1: Sieve analyzer

3.2.2 Banbury mixer

The compounding of rubbers, CTL and other ingredients were prepared using MET-GÜR MG - 4 Banbury mixer (Figure 3.2). Its effective capacity is 1500 g. Mixing was done at 50 ^{o}C and 30 rpm during 10 minutes approximately.

Figure 3.2: Laboratory banbury mixer

3.2.3 Two roll mill

The prepared rubber compound were homogenized by using two-roll mill (Figure 3.3) with dimension D=15 cm and L=30 cm with 30 rpm speed. The distance between the cylinders can be varied from 3 mm to 4 mm depends on the mixing stage.

Figure 3.3: Laboratory two-roll mill

3.3 Equipments for Unvulcanized Rubber

3.3.1 Differential scanning calorimeter (DSC)

Curing peak enthalpies (ΔHc) of the compounds were obtained using a Mettler Toledo DSC1 Star System differential scanning calorimeter (DSC) (Figure 3.4) according to ASTM D3418. DSC was performed to unvulcanized rubber from 25 °C to 250 °C with 10 °C/min heating rate under 1.5 bar nitrogen atmosphere.

Figure 3.4: Differential scanning calorimeter

3.3.2 Moving die rheometer (MDR)

Rheological characteristics were measured using Rheometer MDR 2000 (Figure 3.5), Alpha Technologies (USA) according to ISO 3417 method. As considered peak temperatures obtained by DSC, the temperatures were measured around 160 ^{o}C for all kind of rubber/CTL compounds, hence rheometer test temperature were set to 160 °C and flow behaviors were examined during vulcanization such as cure time, scorch time, maximum and minimum torque etc.

Figure 3.5: Moving die rheometer

3.3.3 Thermal gravimetric analyzer (TGA)

TGA analysis was performed using a Mettler-Toledo TGA/DSC 1 STAR analyzer (Figure 3.6) from 25 °C to 600 °C at a heating rate of 20 °C/min under air and nitrogen atmosphere according to ASTM D6370 method.

Figure 3.6: Thermal gravimetric analyzer

3.4 Equipments for Vulcanized Rubber

3.4.1 Density measuring instrument

Densities of cured compounds were calculated using Mettler Toledo density measuring instrument (Figure 3.7) according to ISO 2781.

Figure 3.7: Density measuring instrument

3.4.2 Abrasion test instrument

Abrasion test was operated by using Devotans Elastomers Abrasion Tester DVT DA6 (see Figure 3.8). Abrasion Rate Index was calculated according to ASTM D 5963.

Figure 3.8: Abrasion test instrument

3.4.3 Hardness testing instrument

Hardness values of samples were measured by using durometer (see Figure 3.9) according to ASTM D2240 methods. Results are in Shore A units. The error margins calculated as ±01 Shore A.

Figure 3.9: Durometer

3.4.4 Universal testing machine

Tensile and tear tests were performed by using Zwick/Roell Universal Test Machine (see Figure 3.10). During tensile test, machine speed was 500 mm/min according to

ASTM D 412 method. Also during tear test, machine speed was 50 mm/min according to ASTM D 624.

Figure 3.10: Universal testing machine

3.4.5 Compression set apparatus

Compressive deformation was measured by using compression set apparatus (see Figure 3.11) according to ASTM D 395. Tests were performed under 25% compression.

Figure 3.11: Compression set apparatus

3.5 Methods

3.5.1 Preparation of compounds

Table 3.1: The receipt of rubber compounds.*

Name	NR	SBR	CTL
NR-REF	100		0
NR-CTL5	100		5
NR-CTL10	100		10
NR-CTL15	100		15
NR-CTL20	100		20
SBR-REF		100	0
SBR-CTL5		100	5
SBR-CTL10		100	10
SBR-CTL15		100	15
SBR-CTL20		100	20
NR/SBR-REF	50	50	0
NR/SBR-CTL5	50	50	5
NR/SBR-CTL10	50	50	10
NR/SBR-CTL15	50	50	15
NR/SBR-CTL20	50	50	20

* Other ingredients were constant for all compounds. CB: 40 phr; process oil: 6 phr; ZnO: 5 phr; Stearic acid: 2 phr; MC wax: 1 phr, IPPD: 1 phr; TMQ: 1 phr; CBS: 1 phr; TMTD: 1.5 phr; sulphur: 1 phr.

3.5.1.1 Compounds with untreated leather

Firstly, chrome shavings were cut into smaller size and were dried in an oven at 80 ^{o}C for 6 hours to remove moisture.

Mesh sizes of leather particles was determined using sieve analyzer. CTL was added to different mesh size of pans from 45 to 2000 μm and it was sifted during 10 minutes. Weights were measured in the pans and weight percentages were determined. All rubber ingredients accurately weighed and fed into banbury (raw gum elastomer, CTL, CB and aromatic oil, activators, antioxidants, accelerators and sulphur, respectively). Compounding process was performed at 50 ^{o}C for approximately 10 minutes. Then, compound was put into two-roll mill to homogenize for 2 minutes. Each rubber compound was prepared 1500 grams approximately. Totally fifteen different compositions were prepared as NR-CTL, SBR-CTL, NR/SBR-CTL, five for each. Uncured rubber compounds were molded 2 mm and 6 mm thickness sheets in the hot press at 160 °C their respective cure times and were prepared for tests.

3.5.1.2 Compounds with neutralized leather

Before chrome shavings were added into rubber compound, they were treated with 1% ammonium solution to neutralize their acidic nature for 72 hours. Then they was dried at room temperature for 48 hours. Remaining processes were the same with untreated rubber compound preparation.

3.5.2 Characterization of compounds

3.5.2.1 Rheological analysis

Rheological properties of compounds such as scorch time (t_{S2}), maximum torque (MH), minimum torque (ML), viscous torque (S”), and tan delta values were obtained using MDR at 160 ^{o}C according to ISO 3417. Measurements were done at least three samples from different parts of uncured rubber compounds and average values were calculated.

Typical cure curve of rubber was given in Figure 3.12.

Extent of cure values give information about curing characteristic of compounds. Extent of cure values were calculated using following expression;

Extent of cure = M_H-M_L (dNm) (3.1)

Cure rate index (CRI) values were calculated using following expression;

$$CRI = \frac{100}{t_{90}\text{-}ts_2} \quad (3.2)$$

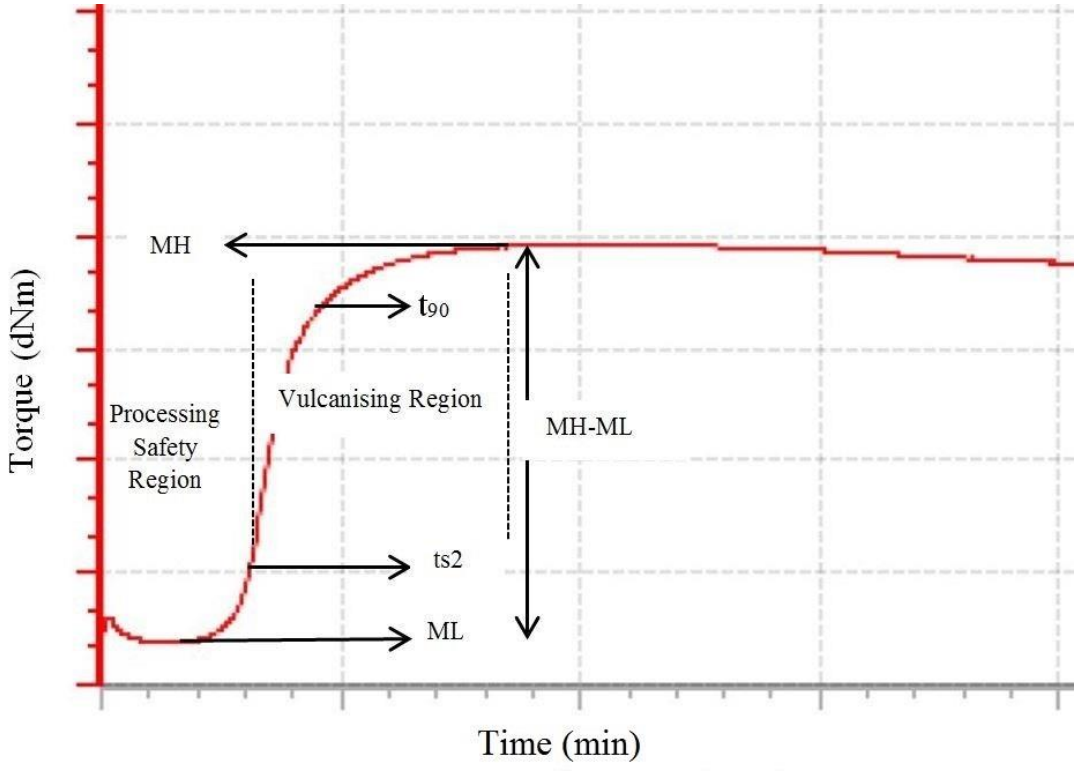


Figure 3.12: Typical cure curve

3.5.2.2 Thermal analysis

Curing peak enthalpies (ΔH_c) values of uncured compounds were obtained using a DSC. Analysis was performed to unvulcanized rubber from 25 °C to 250 °C with 10 °C/min heating rate under ambient air atmosphere and with 1.5 bar nitrogen purge.

Changing on mass by time was measured using TGA. This analysis was performed to unvulcanized rubber from 25 °C to 600 °C with 20 °C/min heating rate under air and nitrogen atmosphere.

3.5.3 Preparation of CTL/rubber samples

The prepared compounds were molded as 2 mm sheets and 6 mm plates by using compression hot press at temperature of 160 °C and based on their t_{100} values of each

one. Sheets were punched to obtain the dumbbell shaped specimens by cutter. At least 8 specimens were used for each compound for tensile and tear tests. Plates were cut to obtain 6 mm test specimens for compression set, hardness tests and abrasion resistance measurements.

3.5.4 Characterization of CTL/rubber samples

3.5.4.1 Abrasion test

Abrasion resistance values of composites were investigated using rotary drum abrasion tester. Specimens with 6 mm thickness and 16 mm diameter were abraded for 40 m. At least five specimens were tested for each compound. Abrasion loss values were calculated in volumetric manner.

3.5.4.2 Compression set test

Recovering ability of rubbers is measured by compression set test. According to ASTM D395 method, 6 mm thickness and 13 mm diameter samples (Figure 3.13) were compressed by 25% of its original thickness and it was held in this state between two steel plate during both at 25 °C for 22 hours and 70 °C for 70 hours for each of the five samples. After compression period was completed, the steel plates were removed and the thicknesses were re-measured.

Compression set values were calculated according to ASTM D395-03 as percentage of original deflection as follow:

$$C_B = [(t_0 - t_i)/(t_0 - t_n)]x100 \quad (3.3)$$

where; C_B is compression set (Test Method B) expressed as percentage of the original deflection, t_0 is original thickness of specimen, t_i final thickness of specimen, and t_n is thickness of the spacer bar used.

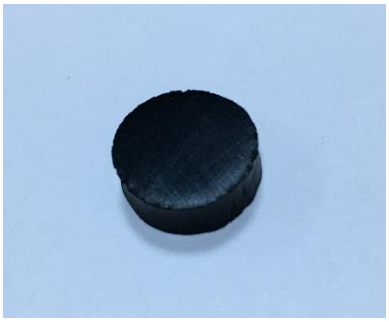


Figure 3.13: Compression set and hardness measurement sample

3.5.4.3 Hardness test

Hardness values of samples were measured by using a Shore A type durometer according to ASTM D2240. After 15 seconds of the beginning of the test, measured values were recorded.

Hardness measurement was done both before and after aging at 70 °C for 70 hours for each sample. For every sample, at least 5 parallel measurements were done. Averages of the values were calculated and recorded.

3.5.4.4 Tear test

Tear strength values of samples (Figure 3.14) were measured by using universal testing machine according to ASTM D 624. Tear test was performed both before and after aging at 70 °C and 70 hours. For every composition, at least 5 parallel measurements were done. Averages of the values were calculated and recorded.

Figure 3.14: Trousers shaped test sample

3.5.4.5 Tensile test

Tensile strength, elongation at break, Young`s modulus, 50%, 100% and %300 moduli values were measured by using universal testing machine according to ASTM D 412. Tensile test was done for at least 5 parallel sample for each composition. Average values were recorded. Tensile test sample was given in Figure 3.15.

Figure 3.15: Dumbbell shaped test sample

4. RESULTS

In this study, CTL was added to NR, SBR and NR/SBR. Rheological, mechanical, thermal and morphological properties before and after aging were studied by adding at various ratios of CTL. Totally fifteen composition were prepared as seen in Table 3.1. All ingredients was compounded in laboratory banbury mixer. In neutralizing process, before adding to rubber, chrome shavings were treated with 1% ammonium solution for 72 hours then dried at room temperature for 48 hours. Then the compound was prepared as five different compositions just for NR.

4.1 Particle Size Analysis

Particle size distribution of CTL was analyzed by sieve analyzer. Analysis was completed by using the method which is given in detail, in Section 3.2.1. Different mesh sizes and weight percentages of CTL particles were shown in Table 4.1.

Table 4.1: Particle size distribution of CTL.

Mesh Size (μm)	CTL (wt.- %)
Pan	0.11
45	0.12
125	6.11
250	15.98
500	32.65
1000	14.15
2000	30.78

Mesh size percentages of CTL were changed between 45-2000 μm. The most used particle size (32.65 wt.-%) was 500 μm and 2000 μm (30.78 wt.-%). Total used mesh sizes of CTL (77.6 wt.-%) changed 500 and 2000 μm.

4.2 Rheological Properties of Compounds

The vulcanization characteristics of all samples were studied using a MDR at 160 ^{o}C. Some parameters such as scorch time, curing time, maximum and minimum torque etc. were obtained from rheometer test.

M_H–M_L tells about information related to curing and crosslink degree of compound. M_L value gives information about indirect measure of the viscosity of compound.

Rheometer curves of all compounds are given in Figure 4.1-4.3. Some important points and calculated cure extent and CRI values are given in Table 4.2.

As seen in Figure 4.1, results show that M_L values of the compounds have been significantly increased for CTL containing compounds. This is because of increasing viscosity in case of CTL incorporation. M_H values were not affected by CTL incorporation; but also M_H–M_L values decreased slightly for CTL containing compounds. This finding shows that, CTL incorporation has only a slight negative effect on crosslink density of the vulcanizates. Another important point is higher cure rate index for NR-CTL compounds. This may be a reason for lower crosslink density due to lower reaction yield between sulphur and the unsaturated sites on NR. Here, it is speculated that chromium cation accompanies the vulcanization activation step in NR vulcanization.

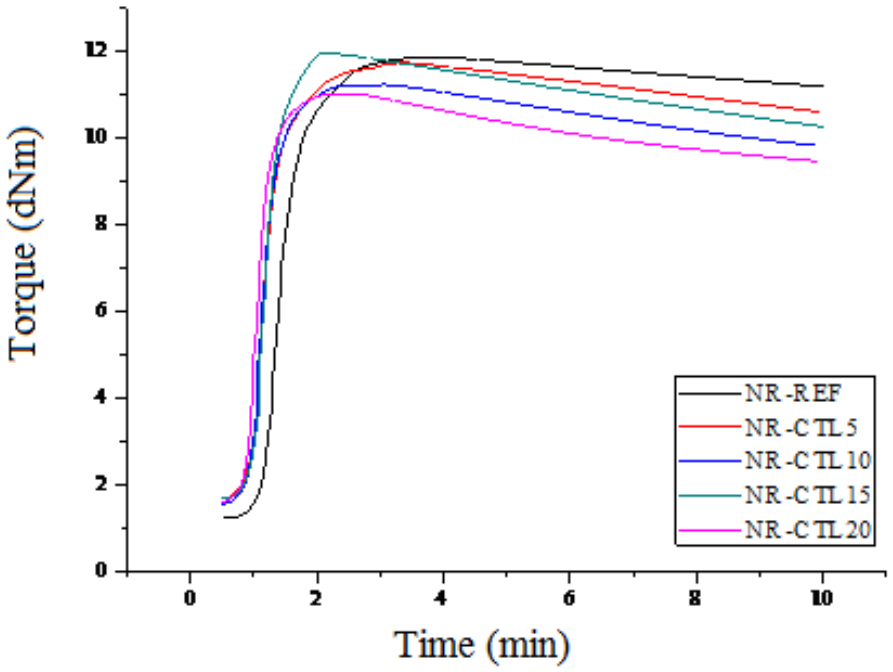


Figure 4.1: The graph of cure curves of NR-CTL compounds

As seen in Figure 4.2, viscosity increment is convenient for SBR-CTL compounds, too. In SBR-CTL compounds, it is also seen from the cure curves that cure extent, so crosslink density, decreased significantly by CTL incorporation. Change in cure rate index for SBR compounds were also quite higher than that of NR compounds. However, decreased crosslink density cannot be explained by only higher reaction

rate phenomena. It is thought that, chromium cation has a different effect on vulcanization activation step for SBR with compared to NR.

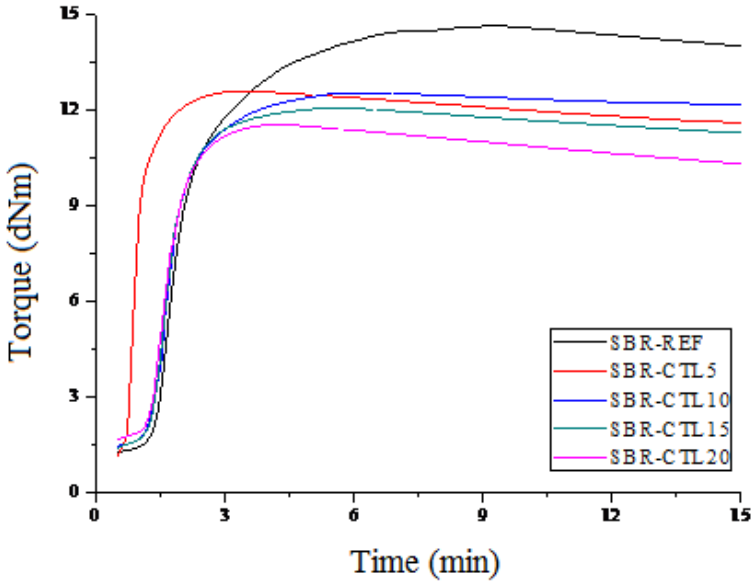


Figure 4.2: The graph of cure curves of SBR-CTL compounds

As seen in Figure 4.3, cure curves have a stable and moderate behavior for NR/SBR-CTL compounds. Decreasing crosslink densities for SBR sites is thought to be suppressed by insensitive NR chains; crosslink density values have been kept in a narrow band. However, higher reaction rate trend for CTL containing compounds and also the presence of NR caused reversion-type behavior for SBR.

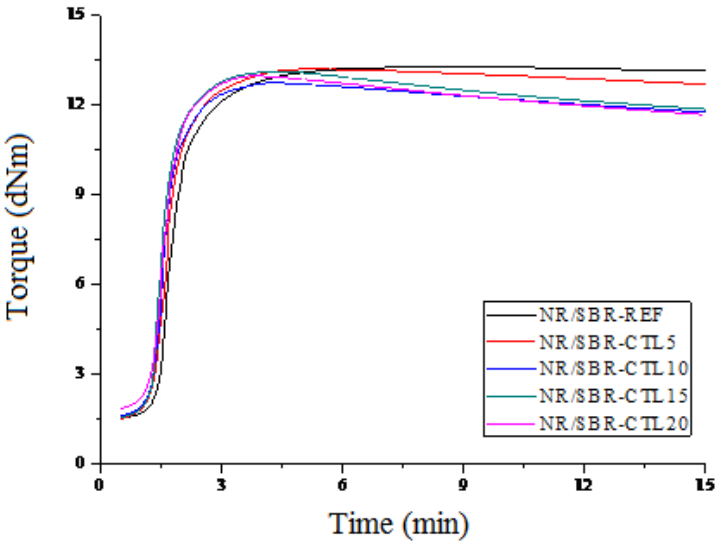


Figure 4.3: The graph of cure curves of NR/SBR-CTL compounds

Table 4.2: Cure extent and CRI values of NR-, SBR- and NR/SBR-CTL.

	Cure Extent (dNm)	CRI	MH (dNm)	ML (dNm)	t_{s2} (min)
NR-REF	10.7	123.5	11.8	1.1	1.2
NR-CTL5	9.7	139.2	11.4	1.6	1.0
NR-CTL10	9.7	197.4	11.3	1.6	1.0
NR-CTL15	10.5	194.9	12.2	1.6	1.0
NR-CTL20	9.4	224.2	11.0	1.6	0.9
SBR-REF	13.4	33.3	14.6	1.2	1.4
SBR-CTL5	12.4	40.3	13.7	1.2	1.4
SBR-CTL10	11.1	67.5	12.5	1.3	1.4
SBR-CTL15	10.6	82.6	12.1	1.4	1.4
SBR-CTL20	10.0	94.3	11.6	1.6	1.3
NR/SBR-REF	11.7	68.0	13.1	1.3	1.4
NR/SBR-CTL5	11.9	80.6	13.4	1.4	1.4
NR/SBR-CTL10	11.4	93.4	12.6	1.5	1.3
NR/SBR-CTL15	11.4	114.9	13.0	1.5	1.3
NR/SBR-CTL20	12.1	108.7	13.3	1.9	1.3

4.3 Mechanical Properties of Composites

4.3.1 Abrasion test

Abrasion tests are performed according to ASTM D 5963. Abrasion loss values were given in Table 4.3. Loading CTL to NR did not affect abrasion characteristic of composites. Nevertheless, on SBR- and NR/SBR-CTL composites CTL adding increased abrasion loss values. This can be explained by different intervals of NR and SBR between leather based flexibility. Flexible leather particles settled on SBR surface are thought to be abraded easier. However, NR behaves similar to leather particles and this behavior prevents separation of two phases during abrasion test. So, in NR/SBR-CTL compounds, NR phase also prevents further abrasion of the vulcanizate in case of increasing CTL loadings.

Table 4.3: Abrasion loss values of NR-, SBR- and NR/SBR-CTL composites.

CTL Content (phr)	Abrasion Loss (%)		
	NR-CTL	SBR-CTL	NR/SBR-CTL
0	10.5	10	11.8
5	11.1	9.5	11.7
10	10.2	12.2	12.4
15	11.5	12.2	11.6
20	10.7	15.4	13.1

4.3.2 Compression set test

Compression characteristics of the composites were measured under 25% compression for 22 hours at room temperature. Compression set test method cover the testing of rubber intended for use in applications in which the rubber will be subjected to compressive stresses in air media. Compression set results were given in Figure 4.4.

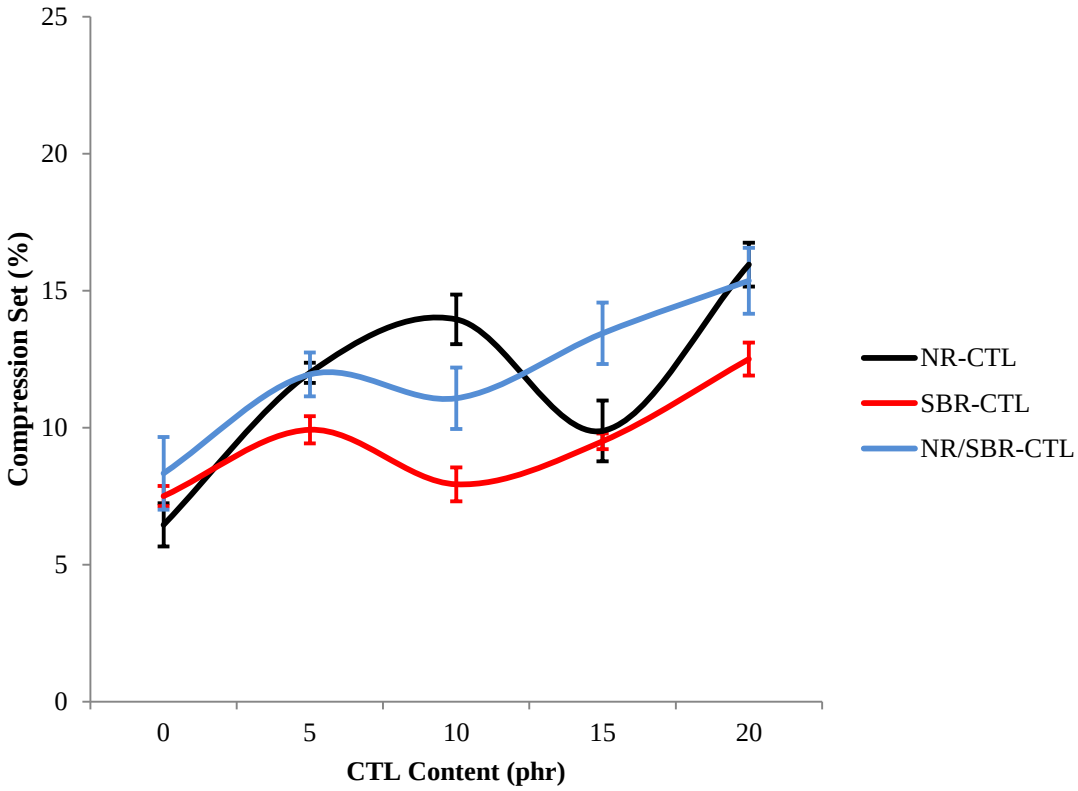


Figure 4.4: Compression set results of NR-, SBR- and NR/SBR-CTL composites

As seen in the figure, CTL addition increased permanent deformation of rubber under compression for all kind of the composites because CTL does not show rubbery behavior due to three-dimensional crosslinked structure. In other words, increasing CTL provides solid-like behavior.

4.3.3 Hardness test

Hardness values of composites showed a slight increment when CTL loaded as seen in Figure 4.5. It can be said that this increment is attributed to become more rigid material for rubbers due to unrubbery structure of leather particles.

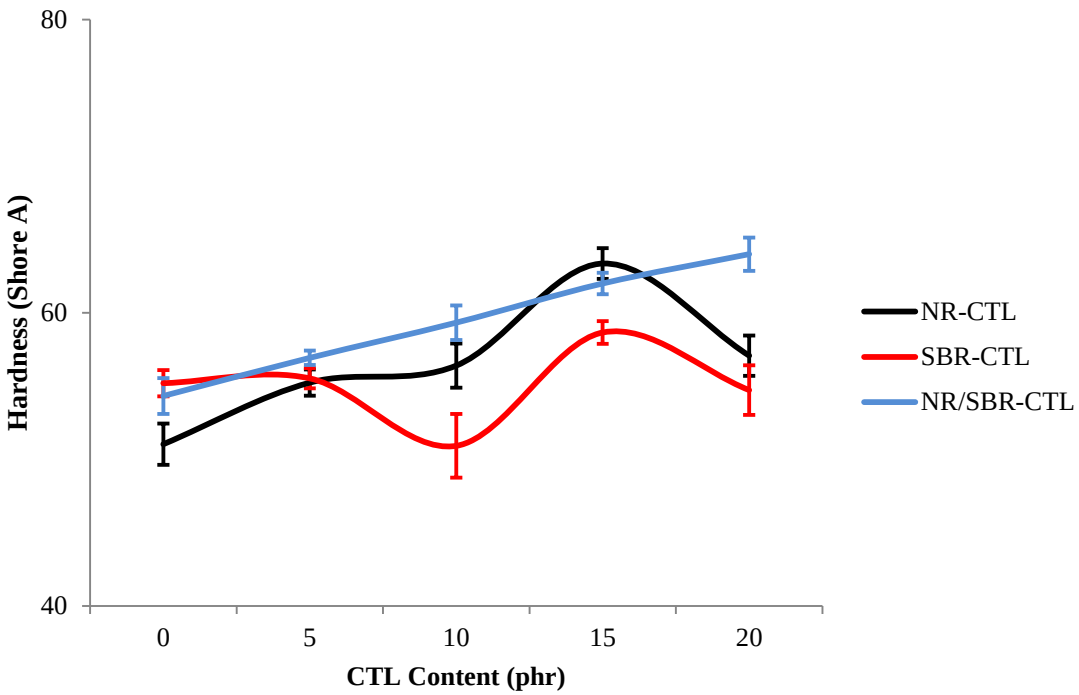


Figure 4.5: Hardness values of NR-, SBR- and NR/SBR-CTL composites

4.3.4 Tear test

Tear strength is the measure of the behavior of material against the growth of crack on materials. In other words, increased tear strength makes material harder to tear.

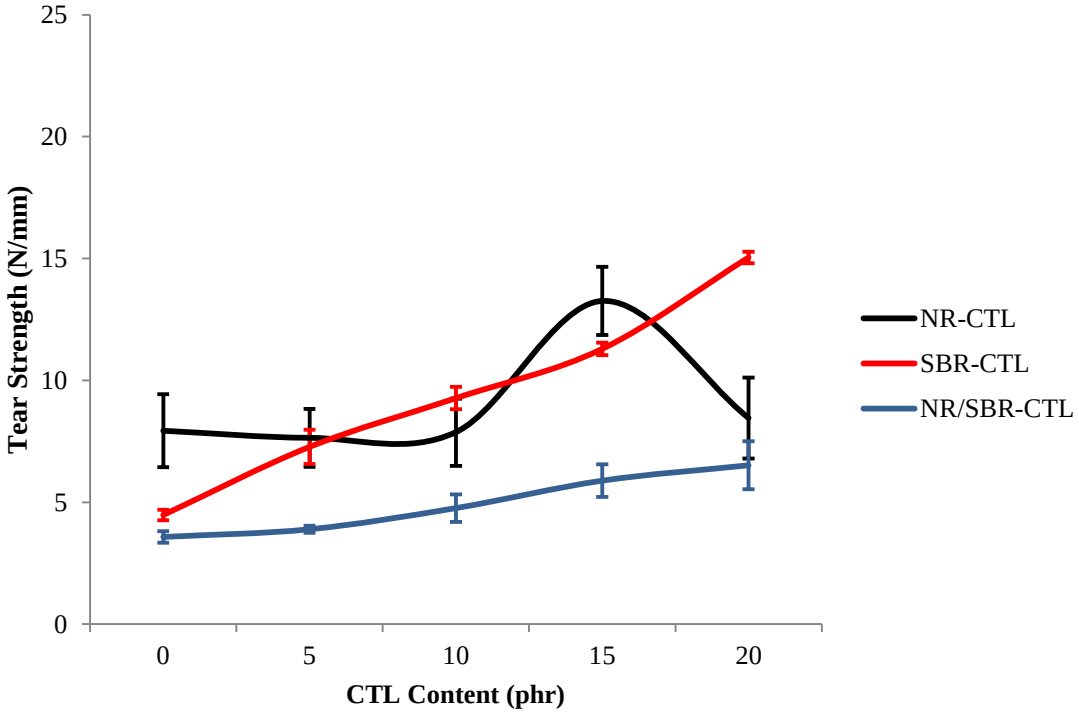


Figure 4.6: Tear strengths of NR-, SBR- and NR/SBR-CTL composites

Figure 4.6 shows the tear strength of CTL/rubber composites. Leather particles increased tear strength of composites due to its 3-D crosslinking structure, and also its producing tortuous way to tear. Possible branched settlement of fibrous leather particles is thought to give enhanced energy dissipation and so enhanced tear properties to NR, SBR and NR/SBR based vulcanizates.

4.3.5 Tensile test

Tensile properties of composites were measured using universal testing machine at the room temperature. Figure 4.7 shows the alterations on tensile strength values with increasing CTL load. In NR compounds, CTL incorporation significantly decreased tensile strength of the vulcanizates due to independent tensile action of CTL in rubber matrix. For SBR-CTL compounds, any significant change was observed in tensile properties.

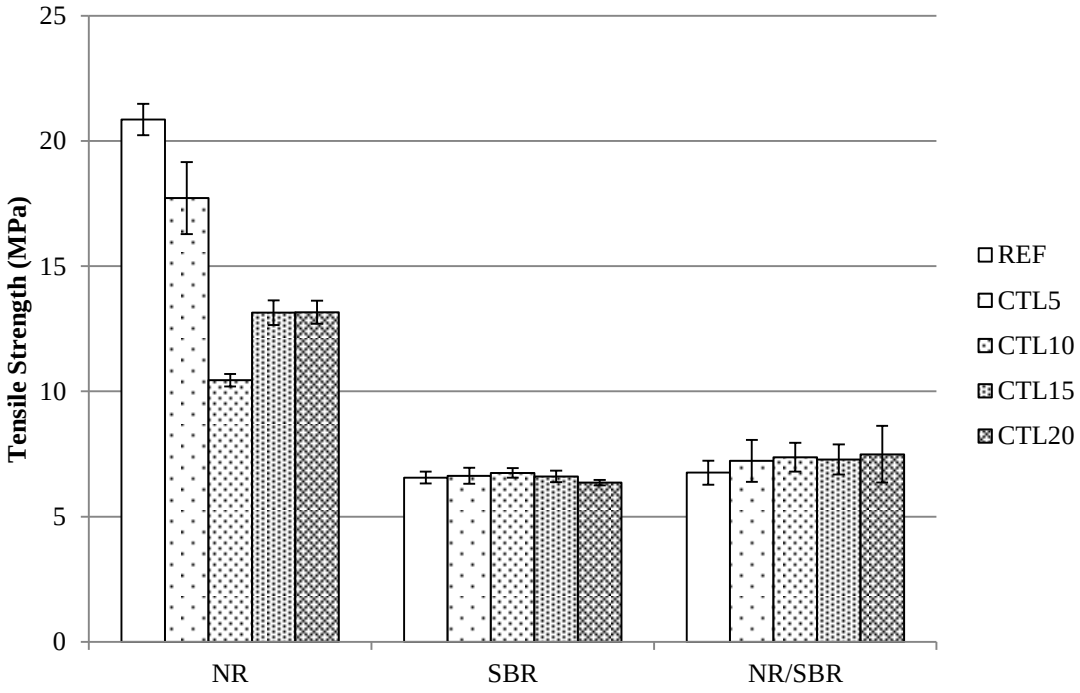


Figure 4.7: Tensile strengths of NR-, SBR-, and NR/SBR-CTL composites

Elongation at break values of composites was given in Figure 4.8. Leather particles caused decreasing on elongation of NR. This may be also attributed to lower tensile strength of CTL containing NR compounds. However, there is a slightly increase in elongation at break values observed for SBR- and NR/SBR-CTL vulcanizates event almost zero change in tensile strength. This trend is due to lower tensile modulus values in case of CTL incorporation and so lower carbon black fraction in the matrix.

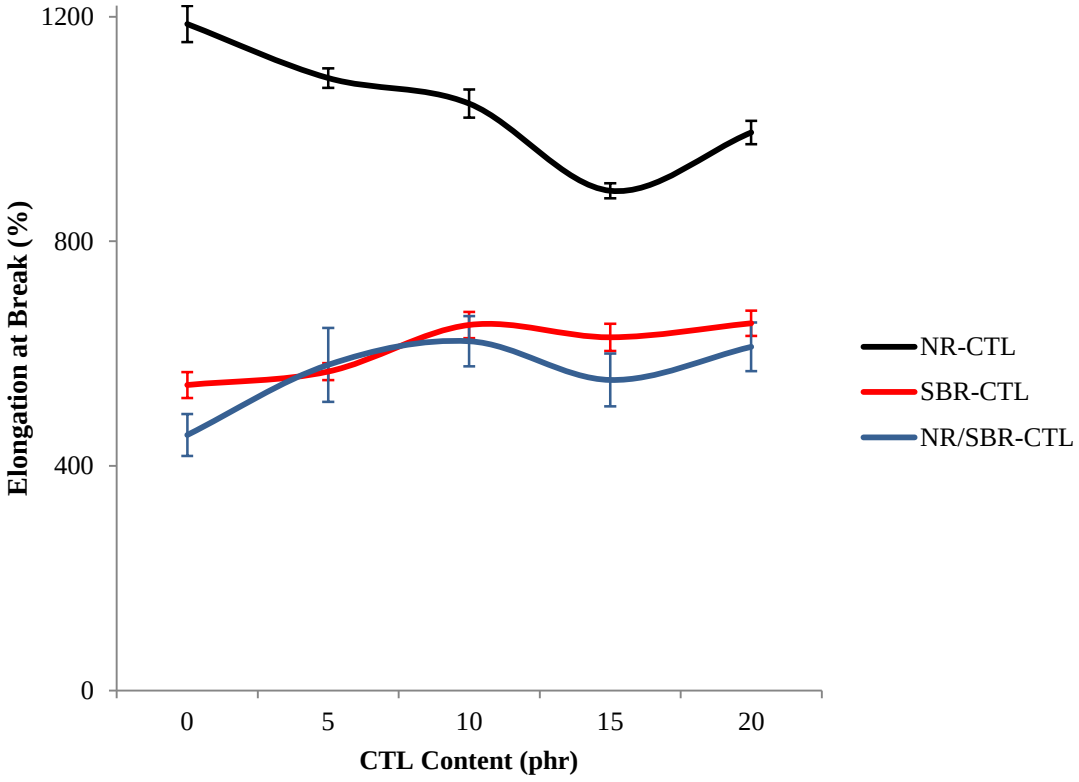


Figure 4.8: Elongations at break of NR-, SBR-, and NR/SBR-CTL composites

4.4 Thermal Properties

4.4.1 Differential scanning calorimeter (DSC)

Curing peak enthalpies (ΔH_c) of the compounds were analyzed by using DSC device. Analysis was done between 25 ^oC and 250 ^oC with 10 ^oC/min heating rate under ambient air atmosphere.

Curing peak enthalpies of compounds with/without CTL were given in Table 4.4 and also in Figure 4.9. As seen from Table 4.4, in NR compounds, increasing CTL content caused higher crosslinking enthalpies, while SBR compounds were giving lower ones. This trend is similar to the rheological properties of the compounds obtained by cure curves. Lower cure enthalpy values for SBR coincide with lower cure extent values in case of higher CTL content. In case of NR/SBR-CTL compounds, decrements in ΔH_c values were diminished due to NR content. Accelerating effect of chromium can also be proved by the starting point shift for crosslinking peaks to the slightly lower temperatures.

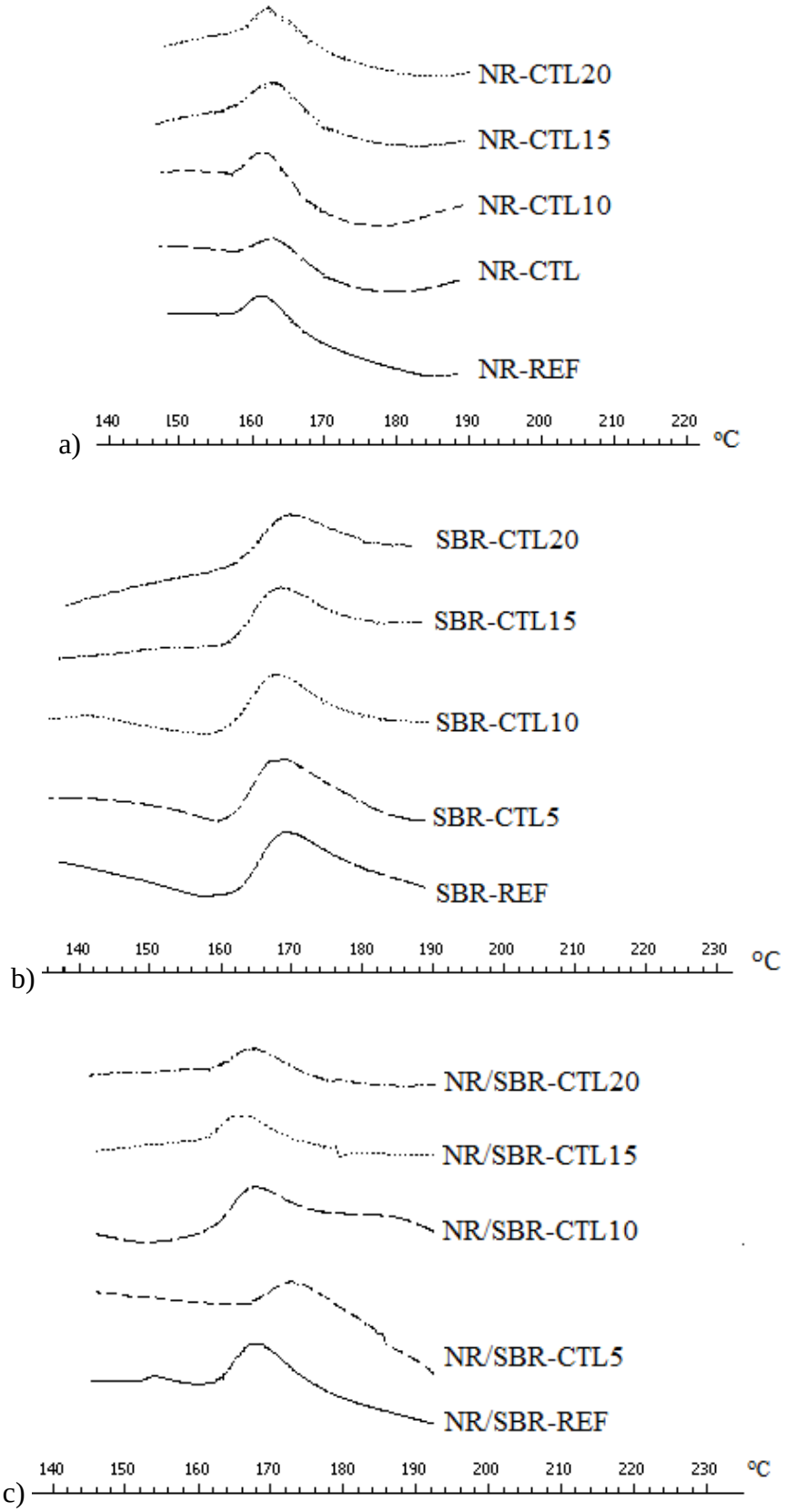


Figure 4.9: DSC thermographs of compounds a) NR-CTL, b) SBR-CTL, c) NR/SBR-CTL

Table 4.4: ΔH_c values of NR-, SBR- and NR/SBR-CTL compounds

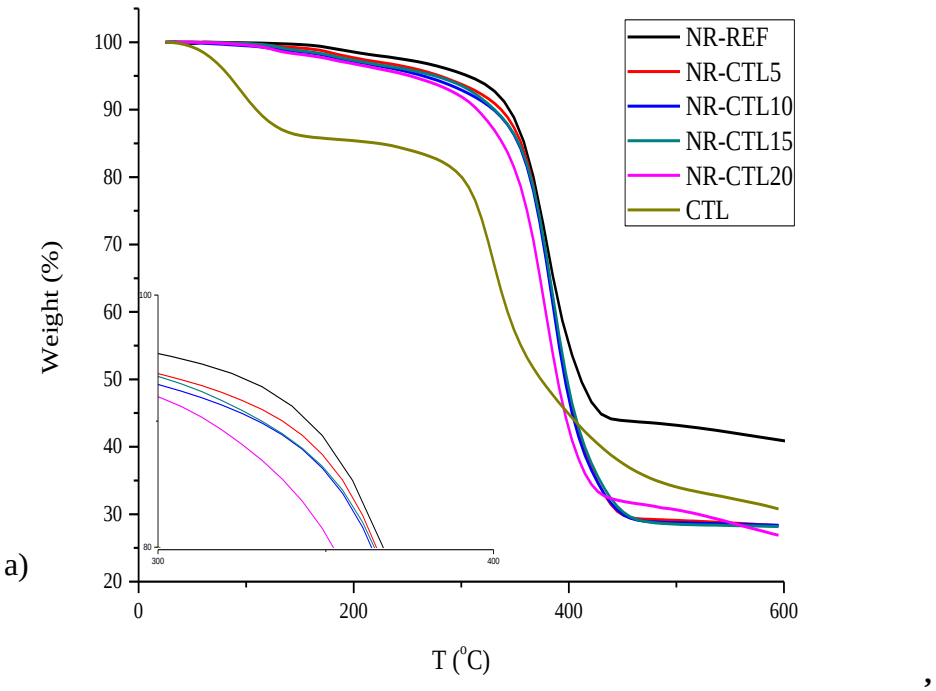
NR-CTL					
CTL (phr)	0	5	10	15	20
ΔHc (J/g)	0.69	0.74	1.05	1.35	1.40

SBR-CTL					
CTL (phr)	0	5	10	15	20
ΔHc (J/g)	4.60	3.25	2.48	2.13	1.73

NR/SBR-CTL					
CTL (phr)	0	5	10	15	20
ΔHc (J/g)	1.62	1.57	1.37	1.12	0.93

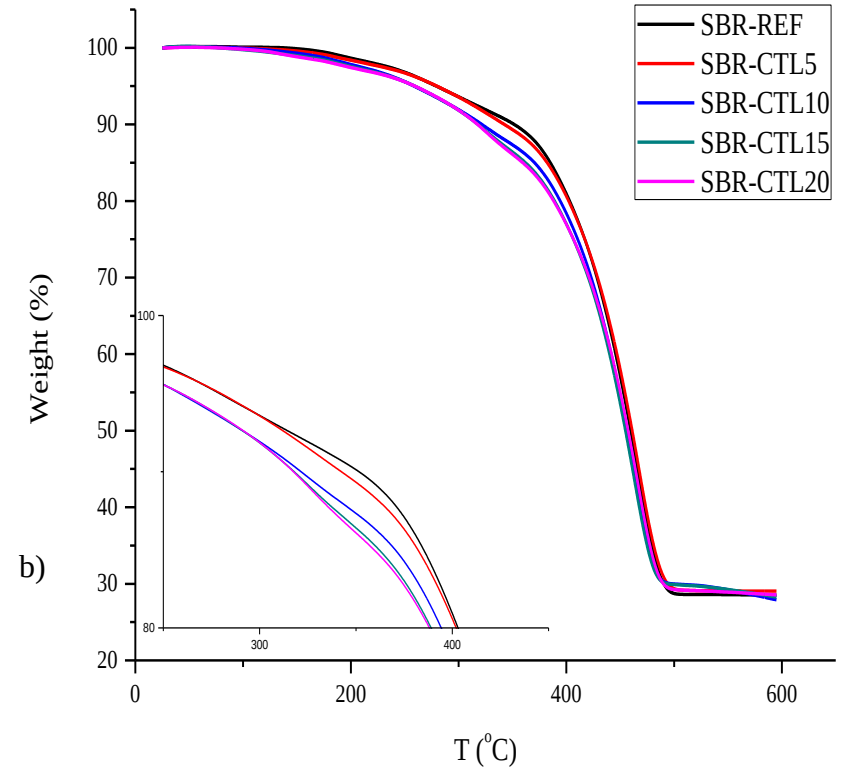
4.4.2 Thermal gravimetric analysis (TGA)

Mass changings of composites were measured using thermogravimetric analysis technique and were shown in Figure 4.10 and Table 4.5. After 100 ^{o}C, a significant mass loss was seen in CTL due to evaporation of humidity, then mass changing started to continue around 320 ^{o}C. As seen in the graph, CTL adding to the rubbers shifted degradation temperature of the vulcanizates earlier and decreased amount of residue after 400 ^{o}C except for SBR composites.



a)

Figure 4.10: TGA thermographs of compounds a) NR-CTL, b) SBR-CTL, c) NR/SBR-CTL



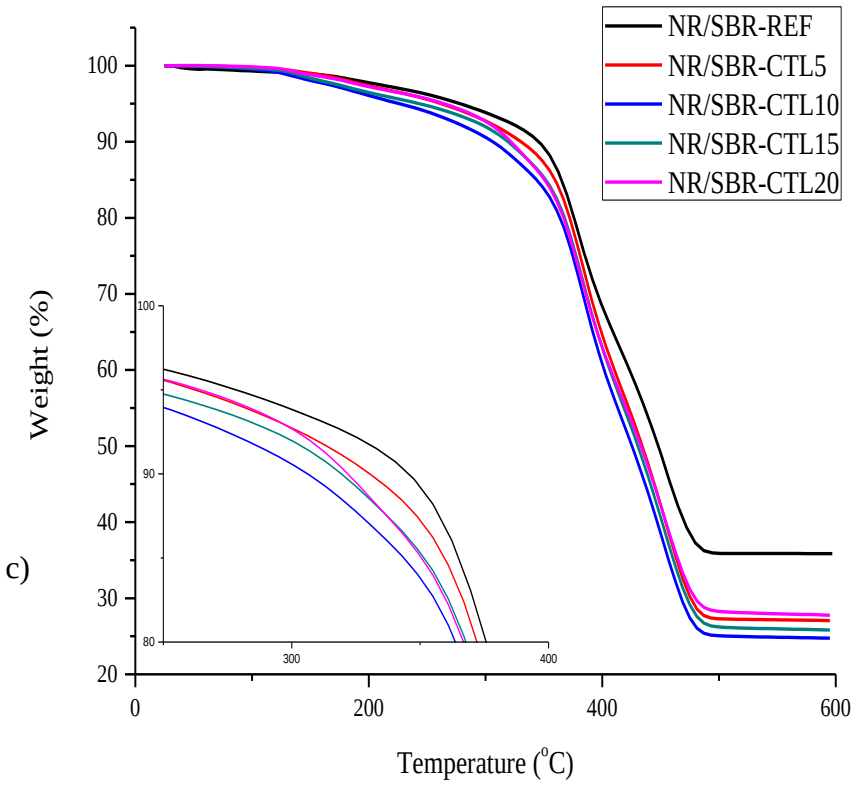


Figure 4.10 (continued) : TGA thermographs of compounds a) NR-CTL, b) SBR-CTL, c) NR/SBR-CTL

Table 4.5: Temperatures of 5%, %10 and 50% mass loss

	T_5 (°C)	T_{10} (°C)	T_{50} (°C)
NR-REF	306	344	411
NR-CTL5	296	343	401
NR-CTL10	287	339	401
NR-CTL15	275	331	398
NR-CTL20	252	315	390
SBR-REF	279	352	460
SBR-CTL5	280	342	461
SBR-CTL10	259	321	456
SBR-CTL15	259	318	455
SBR-CTL20	259	317	457
NR/SBR-REF	278	345	448
NR/SBR-CTL5	262	330	434
NR/SBR-CTL10	226	306	425
NR/SBR-CTL15	243	319	430
NR/SBR-CTL20	264	322	433

4.5 Aging Properties of Samples

4.5.1 Compression set test

Compression set values before and after aging were given below in Figure 4.11, 4.12 and 4.13. For all kind of rubber-CTL composites, permanent deformation of composites increased with adding CTL because CTL do not have rubbery properties. CTL incorporation causes also same trend for hot compression test, independently of the rubber matrix. On the contrary, in the literature, for compression set test CTL did not increase thermal aging resistance (Chronska and Przepiorkowska, 2008).

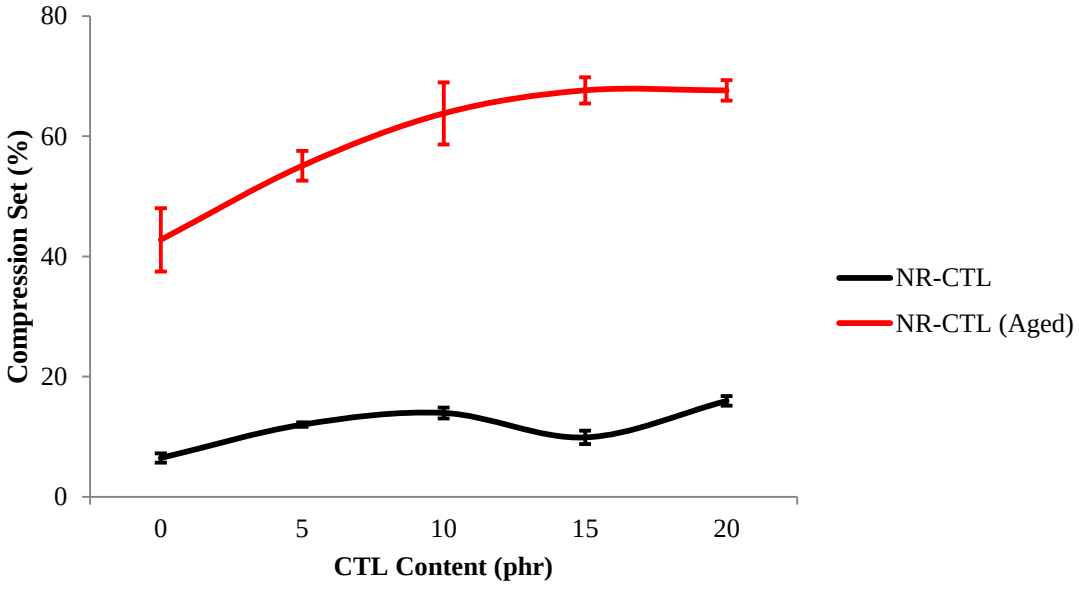


Figure 4.11: Before and after aging compression set values of NR-CTL composites

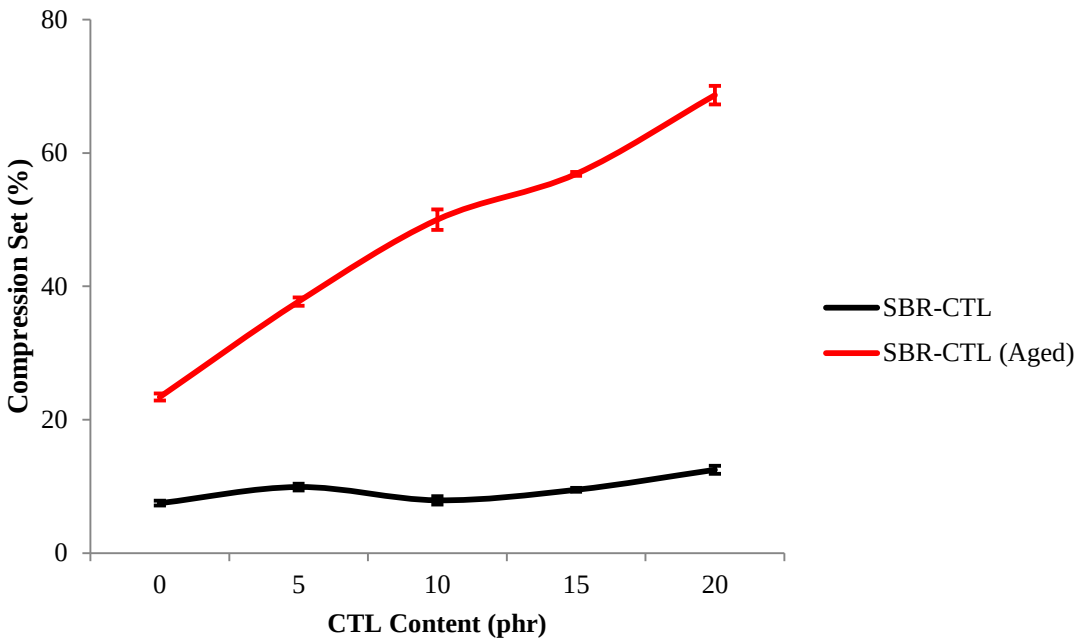


Figure 4.12: Before and after aging compression set values of SBR-CTL composites

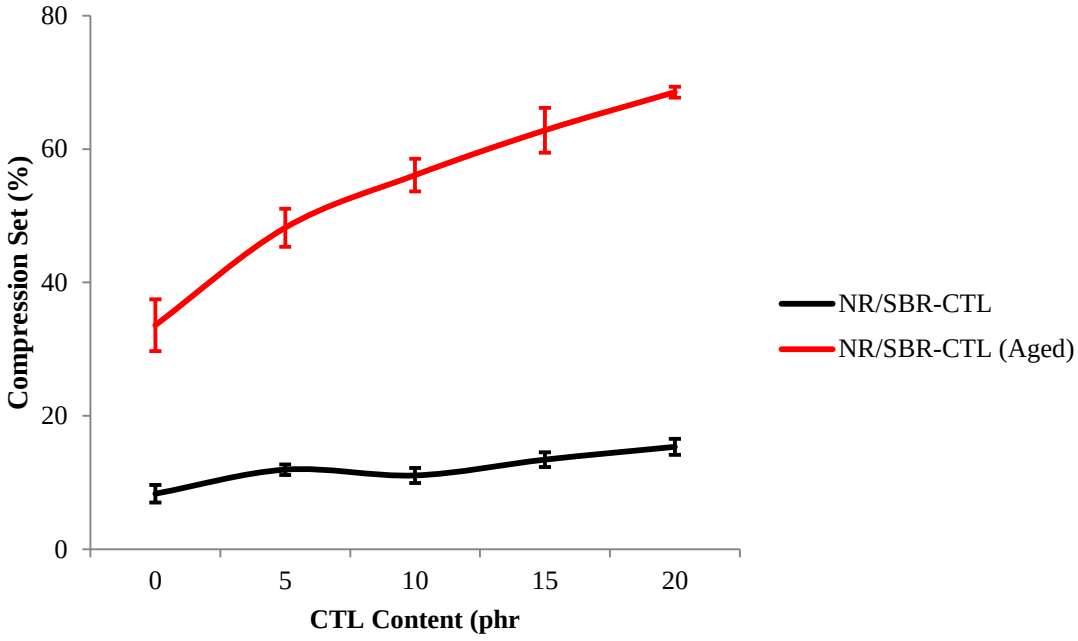


Figure 4.13: Before and after aging compression set values of NR/SBR-CTL composites

4.5.2 Hardness test

As a result of hardness test, loading CTL to rubber composites did not affect thermal aging characteristics of the composites of NR- and SBR-CTL. However hardness

values of NR/SBR-CTL composites did not changed significantly after aging. Results were given in Figure 4.14, 4.15 and 4.16.

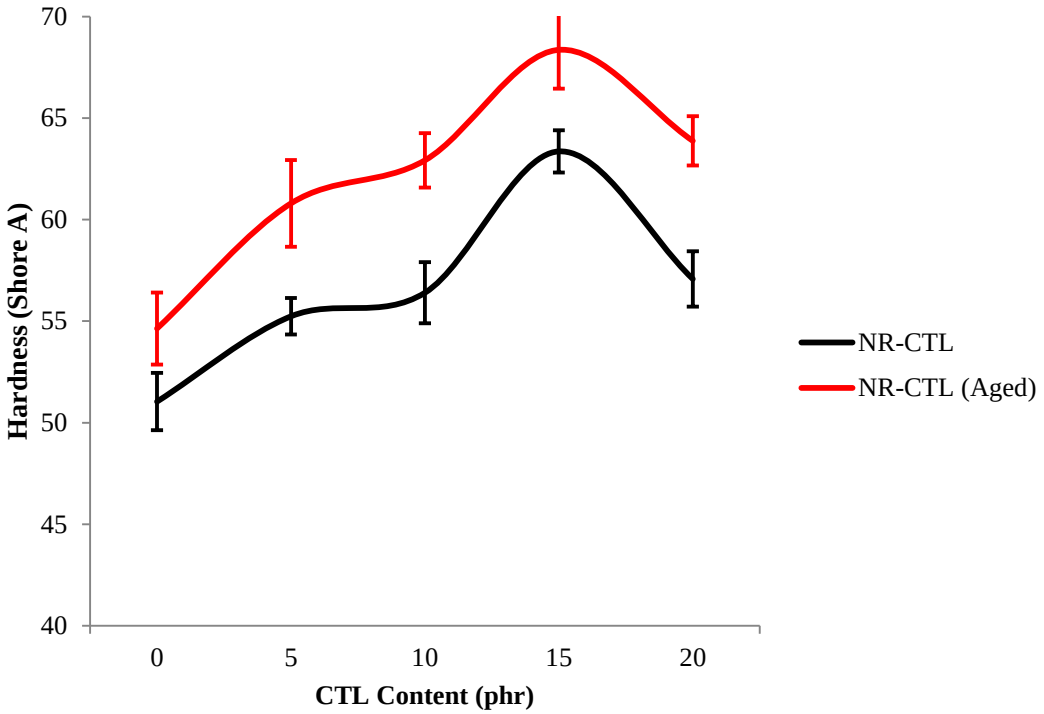


Figure 4.14: Before and after aging hardness values of NR-CTL composites

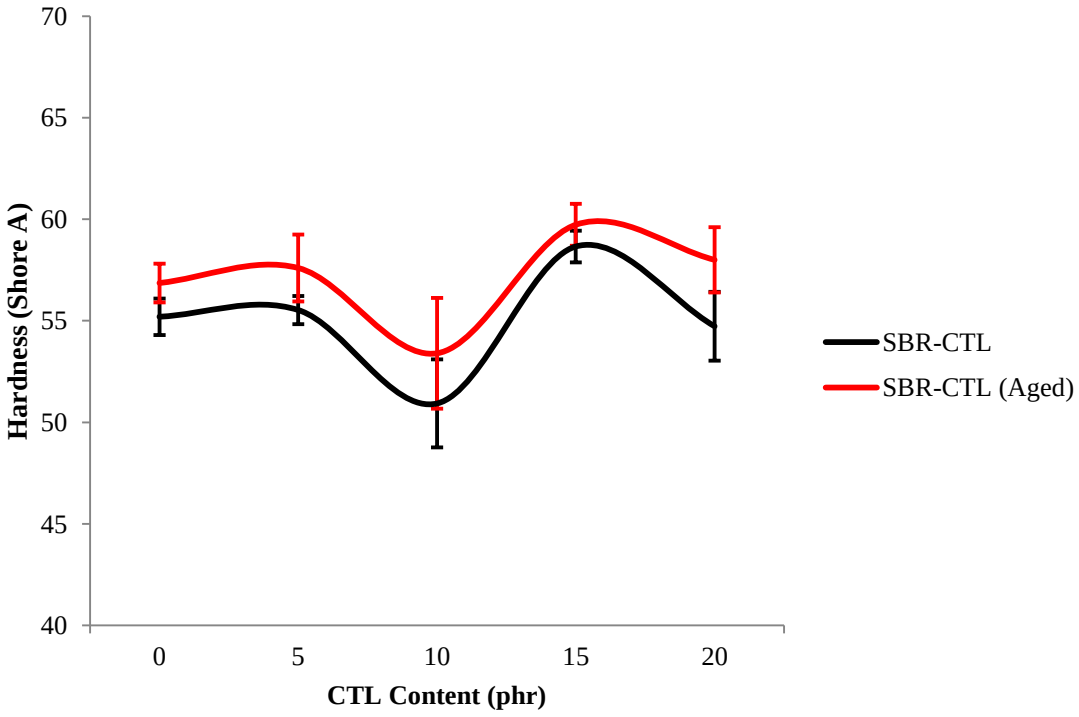


Figure 4.15: Before and after aging hardness values of SBR-CTL composites

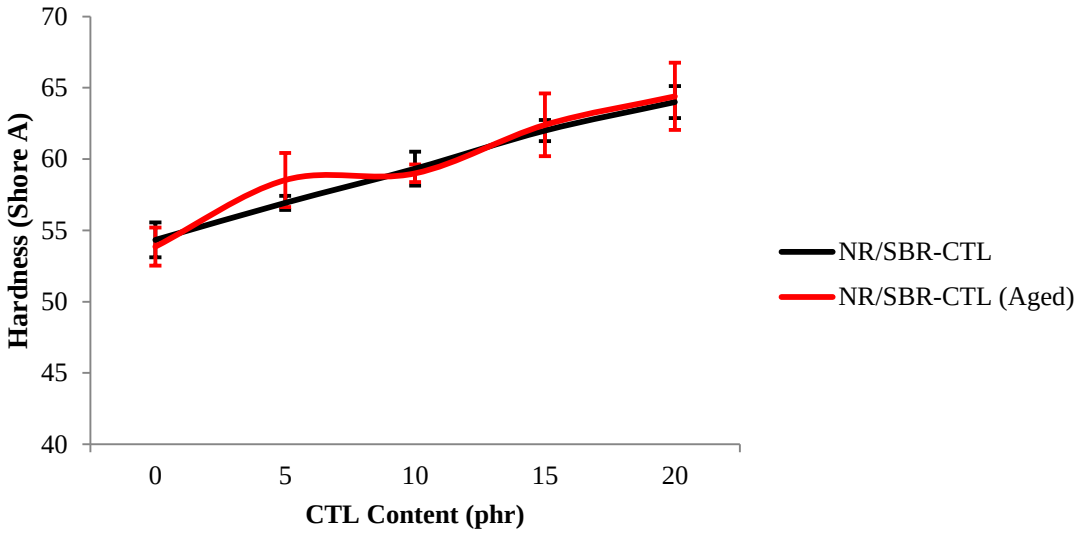


Figure 4.16: Before and after aging hardness values of NR/SBR-CTL composites

4.5.3 Tear test

It was also concluded that one of the most important contributions by CTL incorporation to the rubber matrix was improved tear strength of the vulcanizates. This finding is convenient for all the rubber matrixes. According to tear test results, thermal aging decreased the tear strength of composites as it was expected. However, tear strength values of reference and CTL containing vulcanizates have been affected as almost the same by thermal aging. It may be said that, only for SBR-CTL compounds, increased CTL amounts caused a slight higher deterioration in tear strength values after aging. Results were given in Figure 4.17, 4.18 and 4.19.

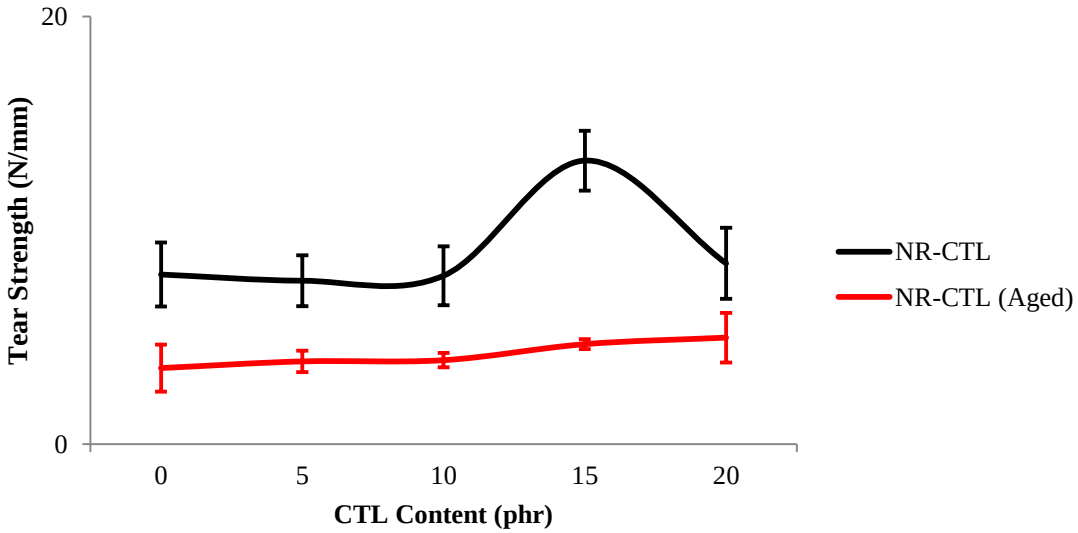


Figure 4.17: Before and after aging tear strength values of NR-CTL composites

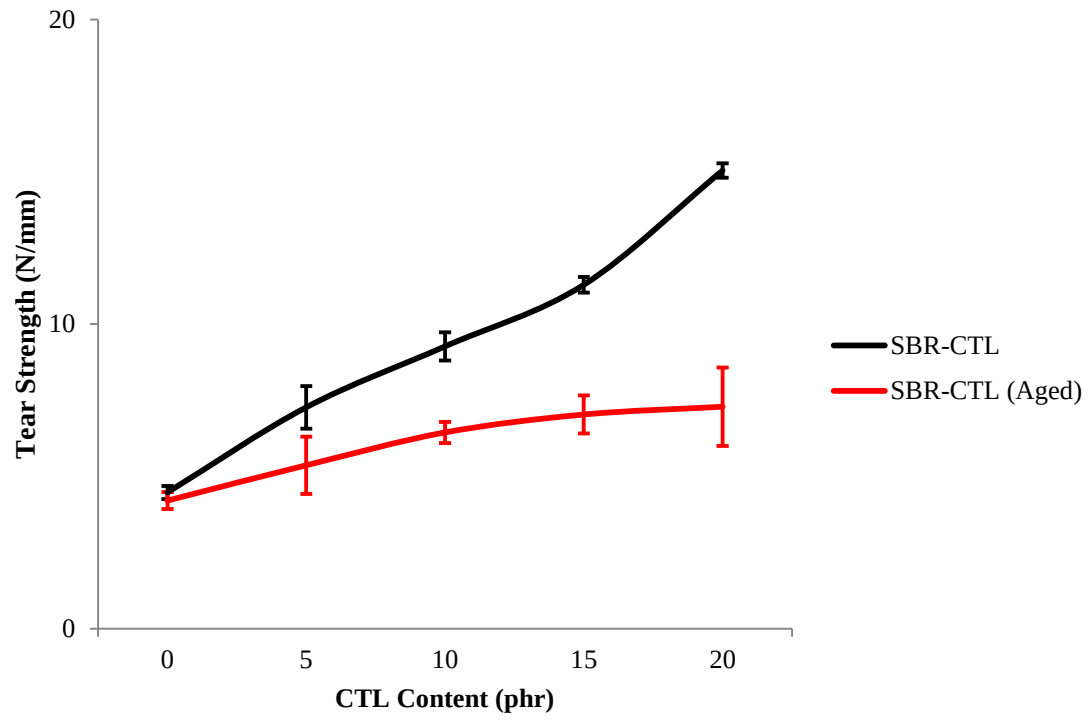


Figure 4.18: Before and after aging tear strength values of SBR-CTL composites

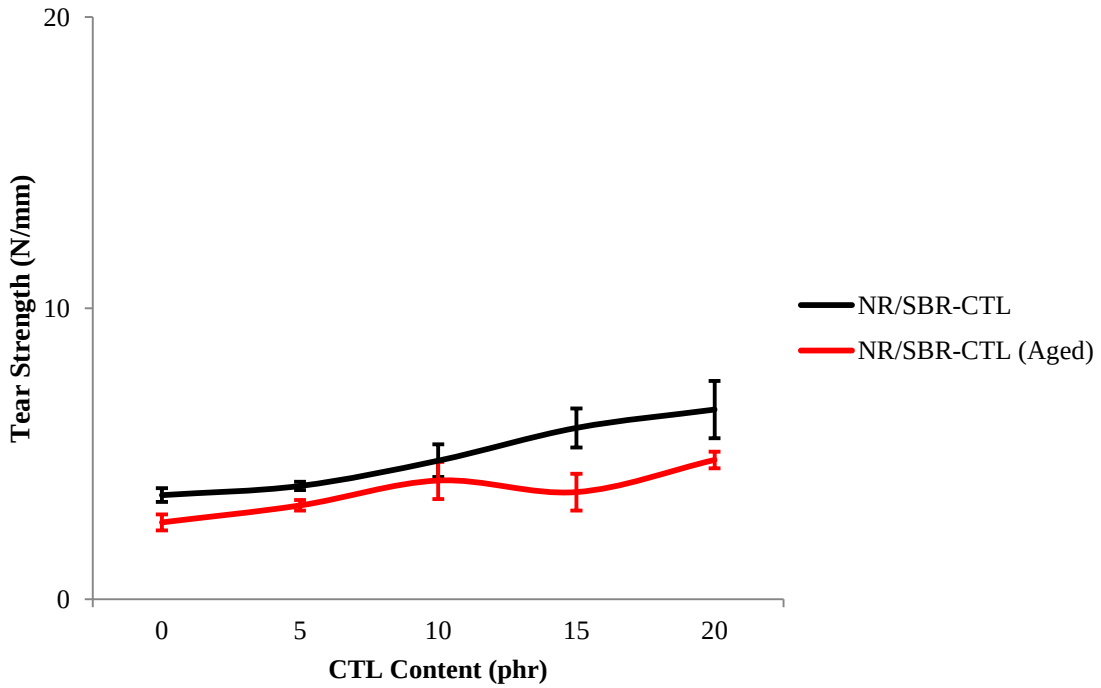


Figure 4.19: Before and after aging tear strength values of NR/SBR-CTL composites

4.5.4 Tensile test

Figure 4.20 shows tensile strength of NR/CTL samples before and after aging. As seen from the figure, it is possible to say that, CTL incorporation improves thermal aging resistance of NR-CTL compounds by means of tensile properties. For SBR containing Rubber-CTL compounds (SBR-CTL and NR/SBR-CTL), there is not a significant change in thermal aging resistance by CTL (Figure 4.21 and 4.22). After this ratio, thermal aging resistance started to decrease. However, increasing CTL content did not affected thermal aging properties of NR/SBR samples (Fig.4.22).

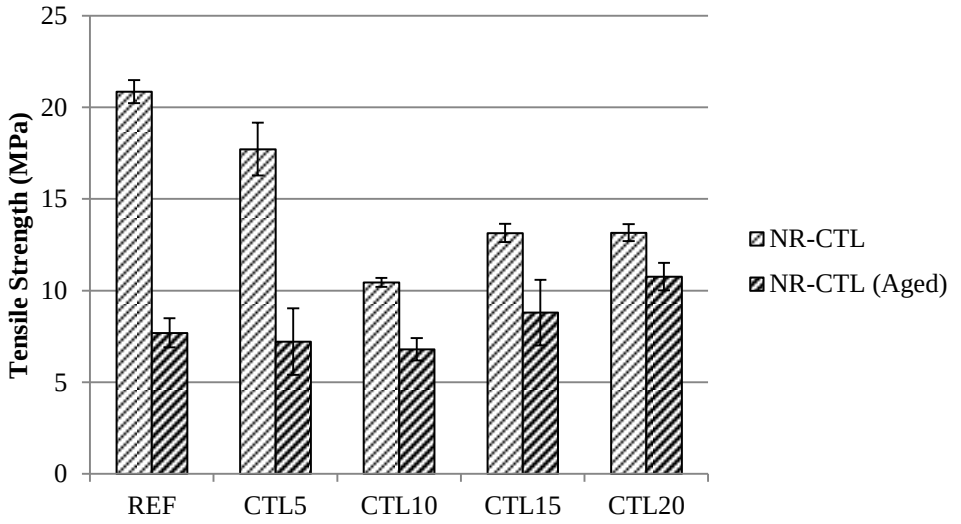


Figure 4.20: Before and after aging tensile strength values of NR-CTL composites

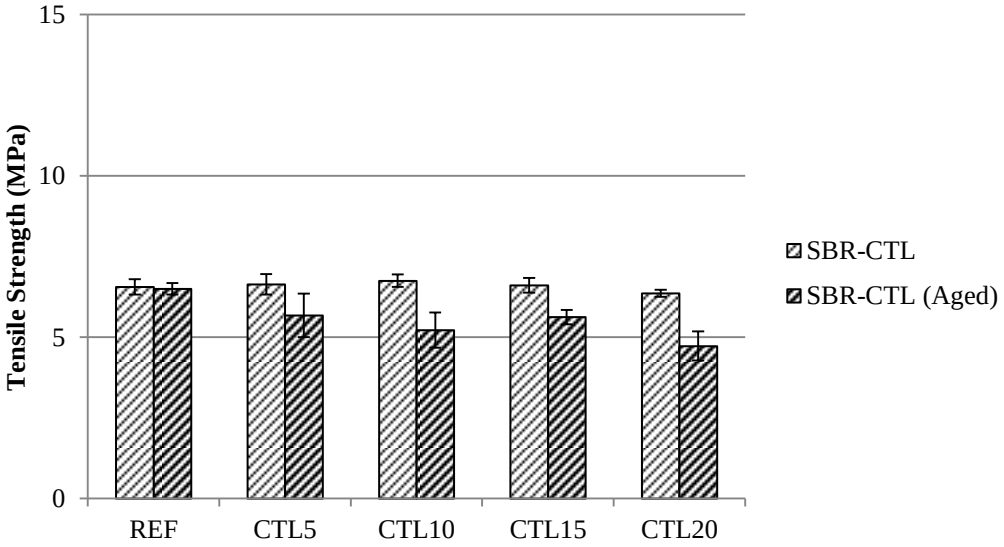


Figure 4.21: Before and after aging tensile strength values of SBR-CTL composites

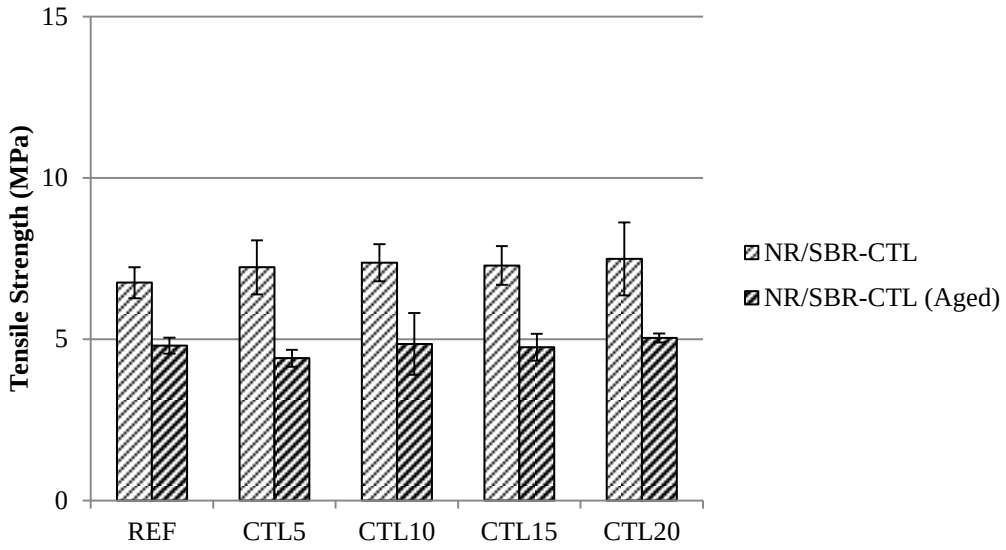


Figure 4.22: Before and after aging tensile strength values of NR/SBR-CTL composites

The effect of CTL on elongation at break of composites also was studied. As seen in Figure 4.23, adding CTL gives narrower gap between elongation limits of aged and unaged vulcanizates. However, similar to tensile strength after aging, for SBR containing Rubber-CTLcompounds (Figure 4.24 and 4.25), CTL incorporation has not a significant effect on elongation behavior. If we consider tensile strength values together with elongation at break values, it is concluded that, CTL incorporation does not affect elastic modulus change for the vulcanizates.

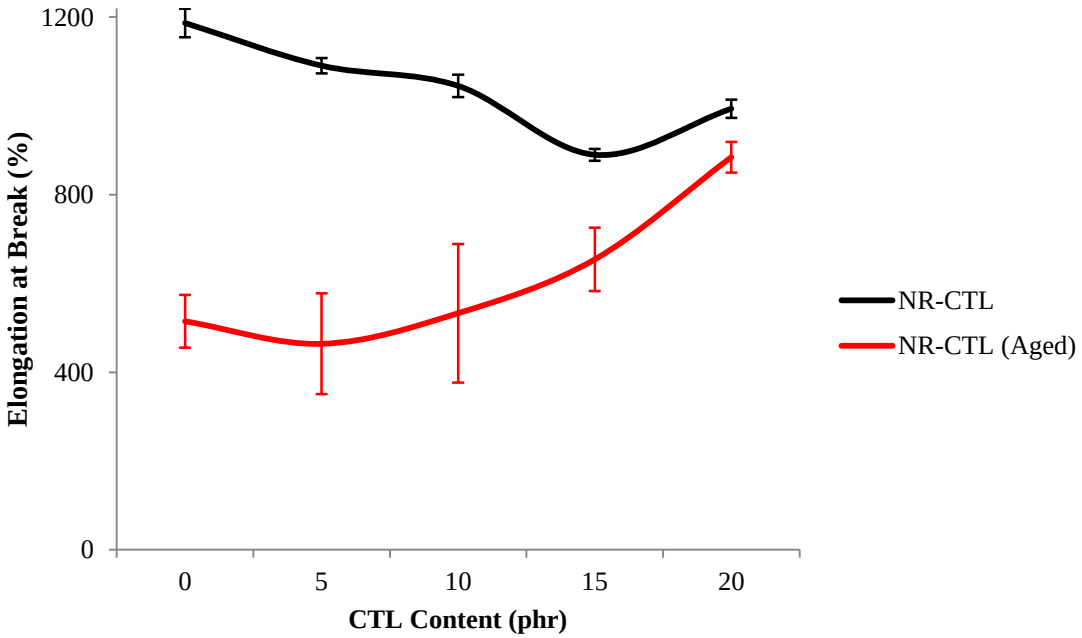


Figure 4.23: Before and after aging elongation values of NR-CTL composites

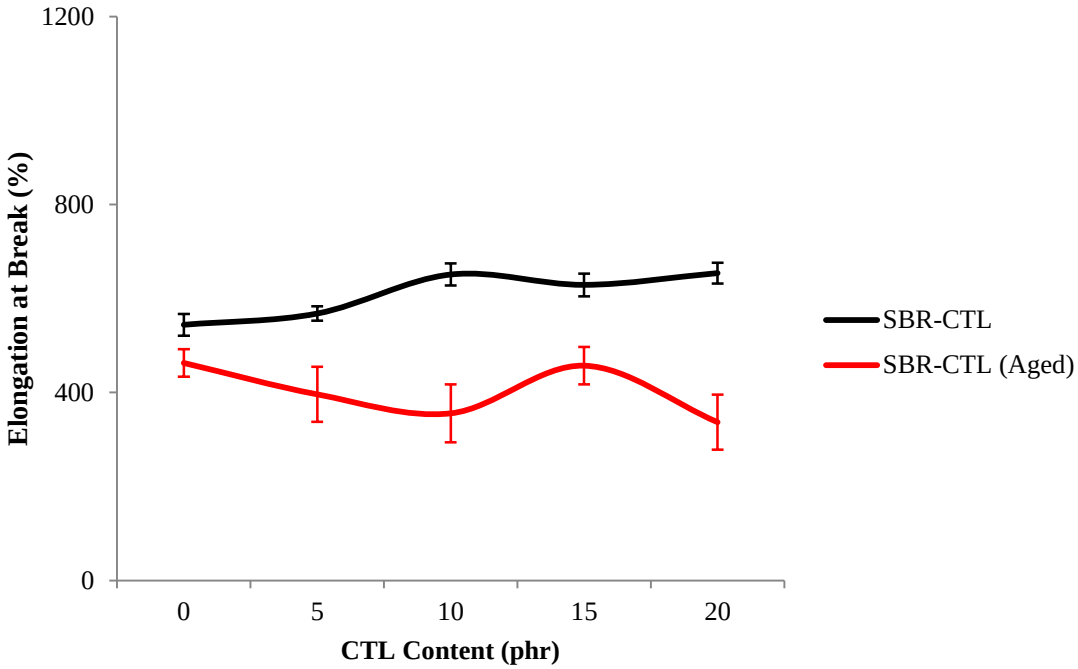


Figure 4.24: Before and after aging elongation values of SBR-CTL composites

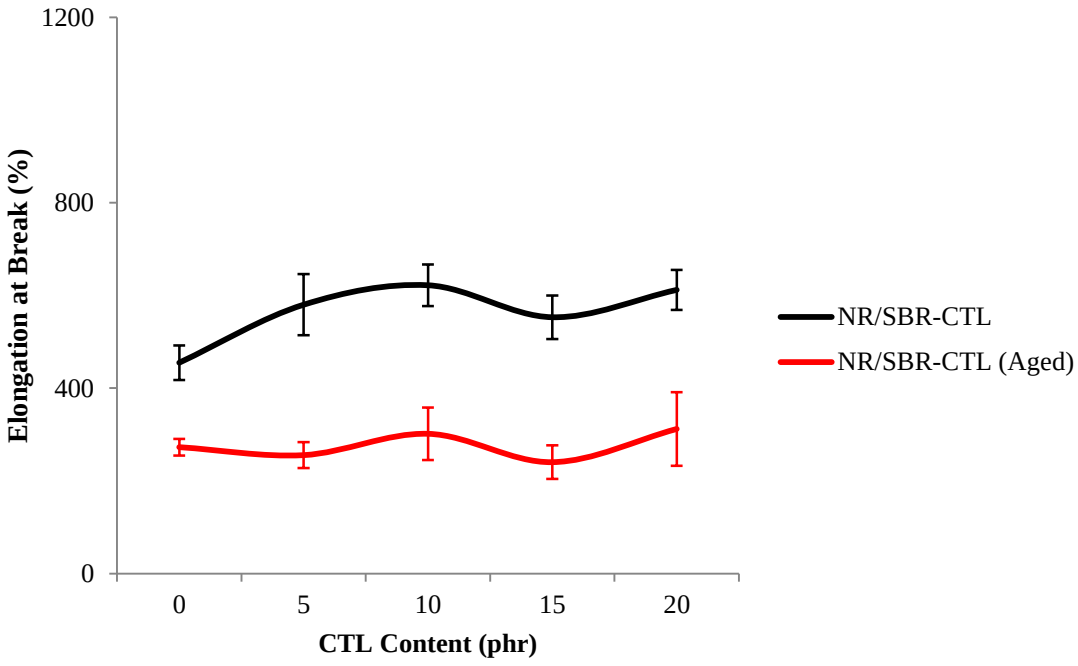


Figure 4.25: Before and after aging elongation values of NR/SBR-CTL composites

4.6 Neutralization Effect on NR-CTL Compounds

In this section, the effect of neutralization process on rheological, thermal, mechanical and aging properties of NR based compounds and composites was

studied. “NRN-CTL” denotation was used for NR based materials containing neutralized leather particles.

4.6.1 Rheological properties of neutralized compounds

The cure curves of NR- and NRN-CTL compounds were shown in Figure 4.26. Cure rate indexes, cure extent, and some important rheological parameters of compounds are also given in Table 4.5. As seen from results, neutralization process increased the cure rate index for NR compounds due to decreased acidic nature of leather containing vulcanization media. However, higher cure rates also gave slightly lower cure extent values. This effect may also be attributed to increased viscosity of neutralized leather containing rubber compounds. In this regard, it may be concluded that, neutralization process affects vulcanization behavior of the compounds but also this phenomena does not have an impressive effect on the resulting crosslinks.

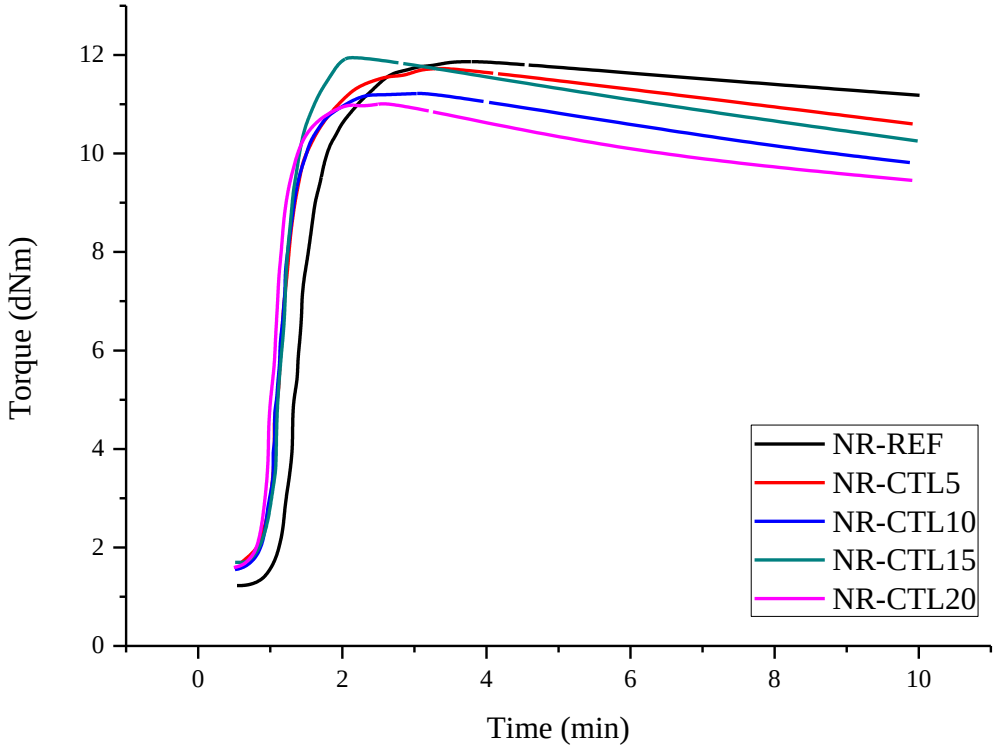


Figure 4.26: The graph of cure curves of compounds a) NR-CTL, b) NRN-CTL

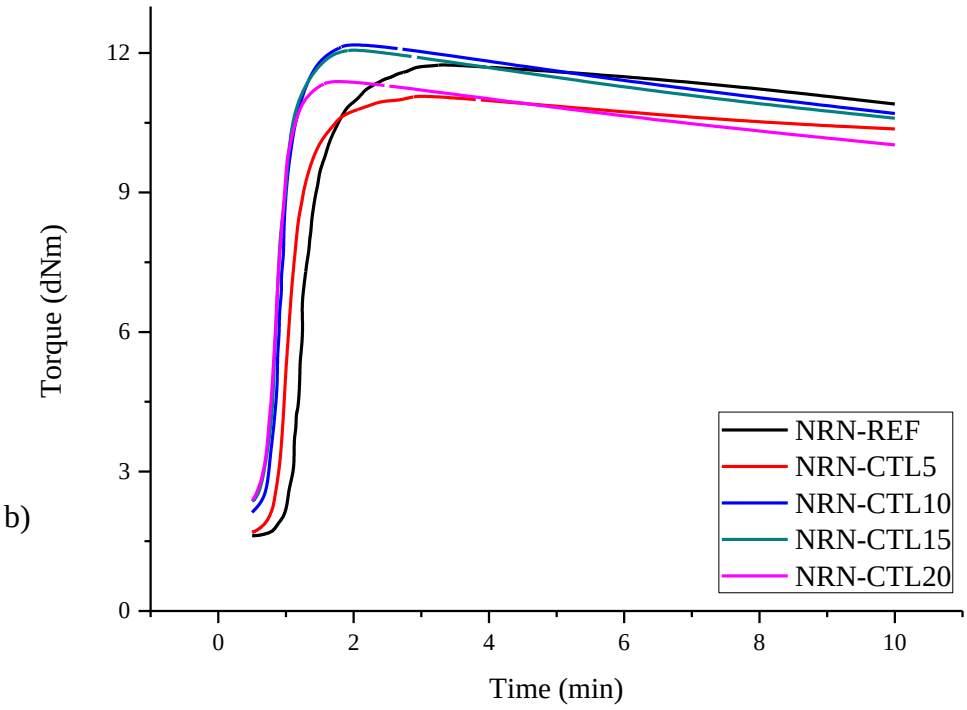


Figure 4.26 (continued): The graph of cure curves of compounds a) NR-CTL, b) NRN-CTL

Table 4.6: Extent of cure and CRI values of NR- and NRN-CTL compounds.

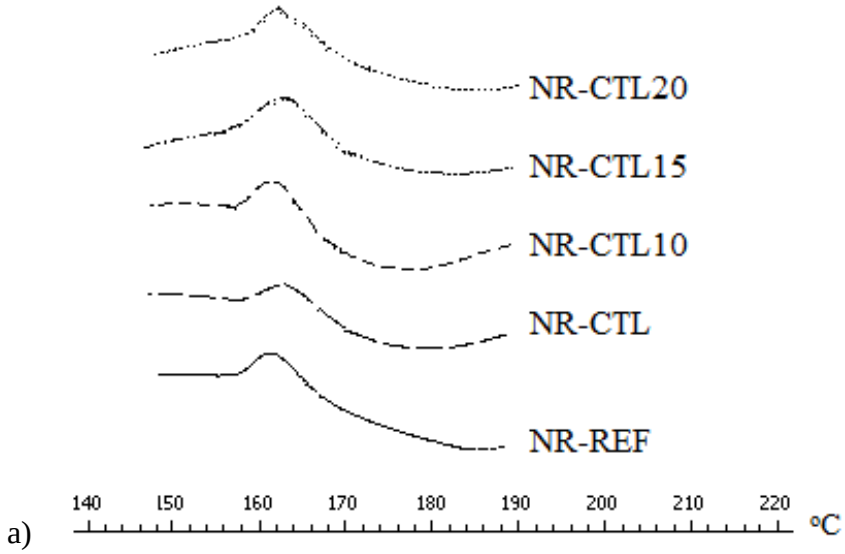
	Cure Extent (dNm)	CRI	MH	ML	ts2
NR-REF	10.7	123.5	11.8	1.1	1.2
NR-CTL5	9.7	139.2	11.4	1.6	1.0
NR-CTL10	9.7	197.4	11.3	1.6	1.0
NR-CTL15	10.5	194.9	12.2	1.6	1.0
NR-CTL20	9.4	224.2	11.0	1.6	0.9
NRN-CTL5	9.6	171.1	11.3	1.7	0.9
NRN-CTL10	9.9	207.1	12.0	2.1	0.8
NRN-CTL15	9.8	240.0	12.1	2.3	0.8
NRN-CTL20	9.1	265.5	11.6	2.4	0.7

4.6.2 Thermal properties of neutralized composites

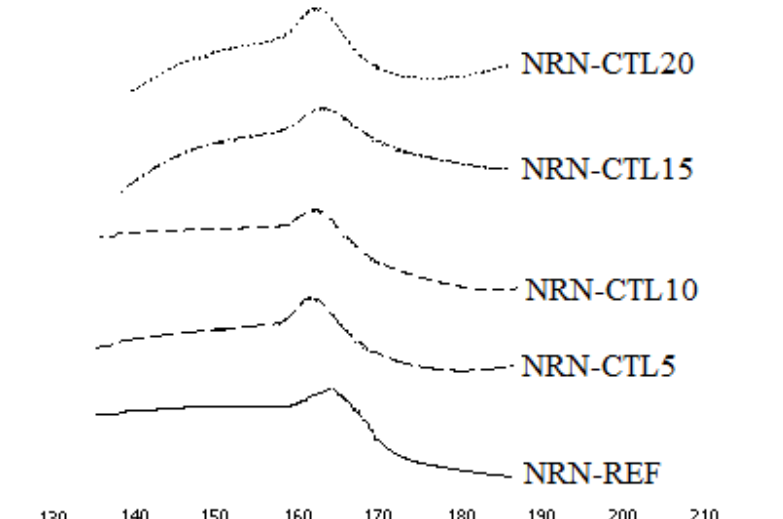
4.6.2.1 Differential scanning calorimeter (DSC)

DSC thermographs of NR- and NRN-CTL compounds were given in Figure 4.27. ΔH_c values of NR- and NRN-CTL compounds were given in Table 4.6. As seen in the figure, crosslinking peaks were observed around 160 ^oC and neutralization process did not shift the vulcanization peak temperature. Nonetheless, ΔH_c values (Table 4.6)

of the compounds increased by neutralization process due to possible effect on the vulcanization reaction mechanism.



a)



b)

Figure 4.27: DSC thermographs of compounds a) NR-CTL, b) NRN-CTL

Table 4.7: ΔH_c Values of NR- and NRN-CTL Compounds.

	NR-CTL					NRN-CTL				
	0	5	10	15	20	0	5	10	15	20
ΔHc (J/g)	0.69	0.74	1.05	1.35	1.40	0.69	1.68	1.78	1.96	2.39

4.6.2.2 Thermal gravimetric analysis (TGA)

The neutralization process did not have any significant effect on result of thermal gravimetric analysis of NR based compounds, as expected. TGA thermographs were shown in Figure 4.28 and Table 4.8, for validating the expectations.

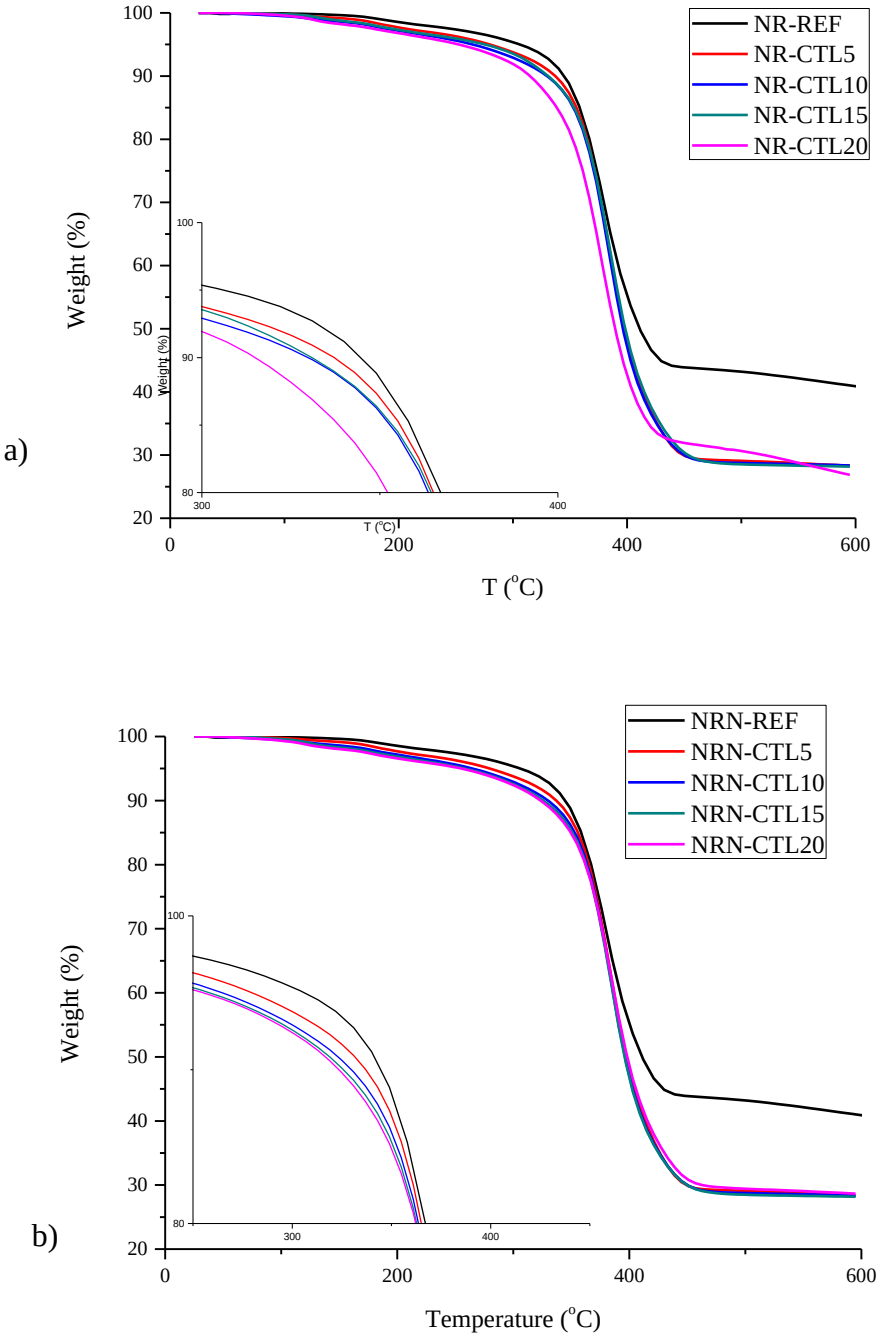


Figure 4.28: TGA thermographs of compounds a) NR-CTL, b) NRN-CTL

Table 4.8: Temperatures of 5%, 10% and 50% mass loss

	T_5 (°C)	T_{10} (°C)	T_{50} (°C)
NR-REF	306	344	411
NR-CTL5	296	343	401
NR-CTL10	287	339	401
NR-CTL15	275	331	398
NR-CTL20	252	315	390
NRN-CTL5	280	337	397
NRN-CTL10	265	330	396
NRN-CTL15	258	326	396
NRN-CTL20	255	323	398

4.6.3 Mechanical properties of neutralized composites

4.6.3.1 Abrasion test

The neutralization process slightly increased abrasion loss of the composites, especially for higher CTL loadings. This trend is attributed to higher hardness values of the relevant compounds (Look at Section 4.6.3.3).

Table 4.9: Abrasion Loss Values of NR- and NRN-CTL Composites.

CTL Content (phr)	Abrasion Loss (% wt.)	
	NR-CTL	NRN-CTL
0	10.5	10.5
5	11.1	11.0
10	10.2	12.9
15	11.5	13.2
20	10.7	14.4

4.6.3.2 Compression set test

Compression set values were given in Figure 4.29. As mentioned before (Section 4.3.2.), adding CTL increased permanent deformation of composites due to the non-elastic nature of itself. This trend is also found as convenient for neutralized compounds.

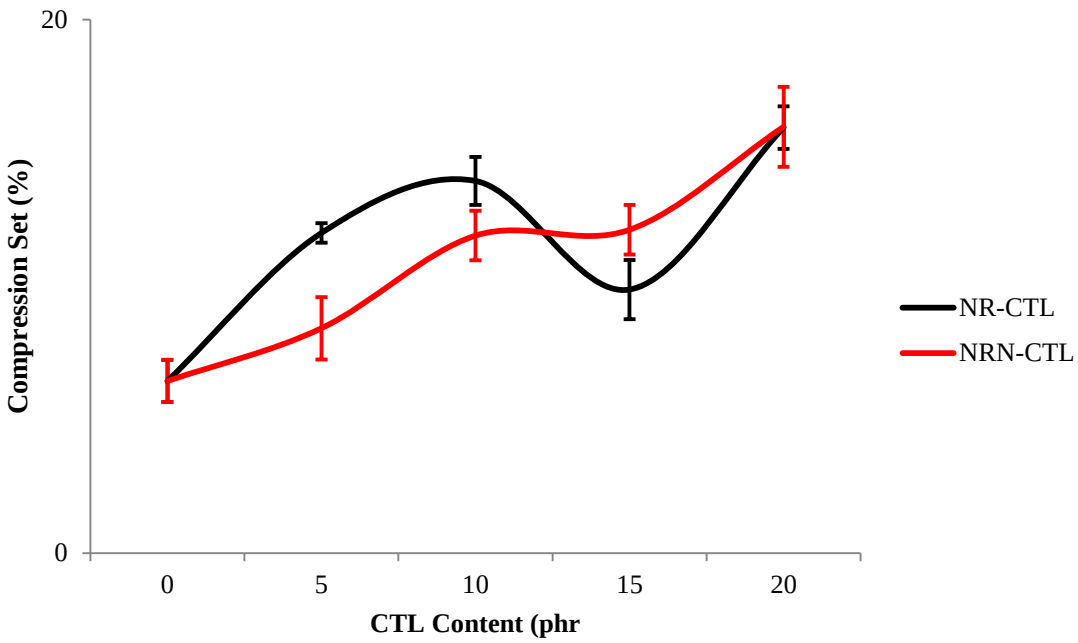


Figure 4.29: Compression set results of NR- and NRN-CTL composites

4.6.3.3 Hardness test

Hardness values of NR- and NRN-CTL composites were compared in Figure 4.30. Neutralized leather particles provided higher hardness values probably due to different vulcanization mechanism, especially moderate CTL containing vulcanizates.

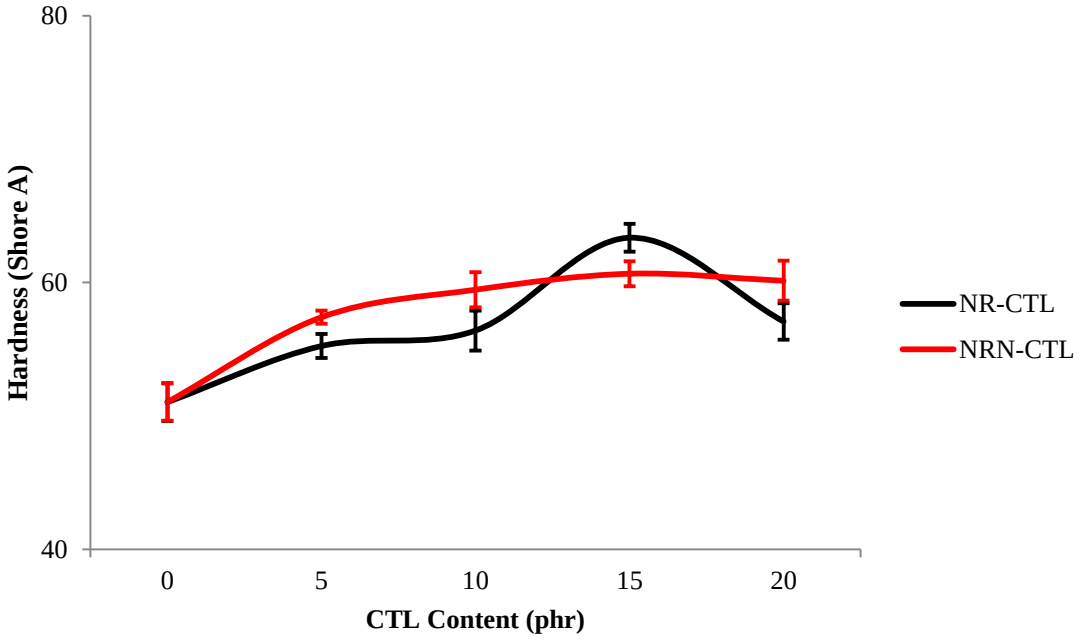


Figure 4.30: Hardness values of NR- and NRN-CTL composites

4.6.3.4 Tear test

The tear strengths of NR- and NRN-CTL composites were shown in Figure 4.31. It is concluded that, neutralization process decreased tear strength of NR based composites as a result of deteriorated tensile properties given in Section 4.6.2.3.

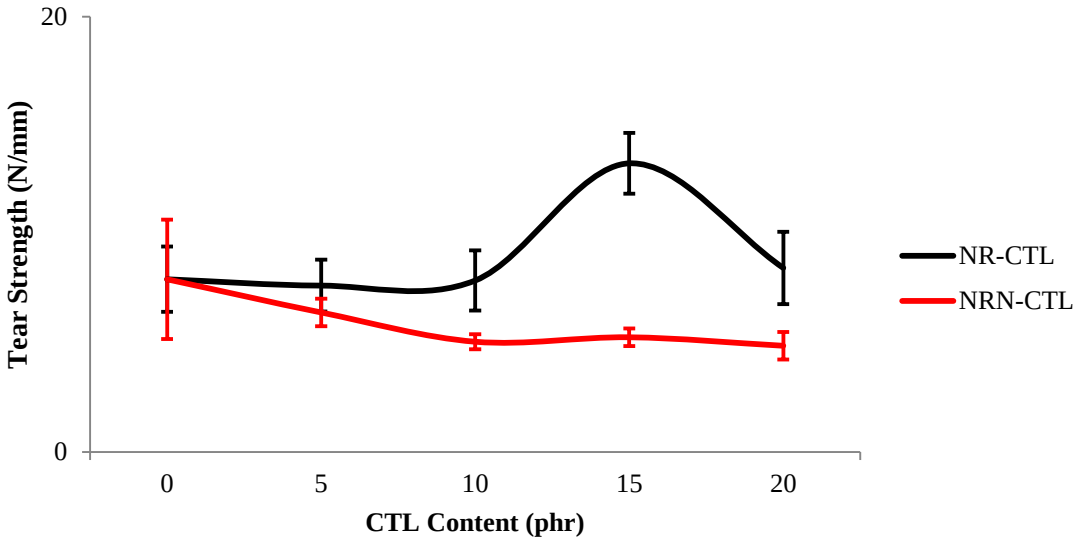


Figure 4.31: Tear strengths of NR- and NRN-CTL composites

4.6.3.5 Tensile test

Tensile strength and elongation at break values of NRN-CTL vulcanizates were shown in Figure 4.32 and 4.33, respectively. As seen in the figures, neutralization process could not improve the tensile properties of the NR based compounds, systematically.

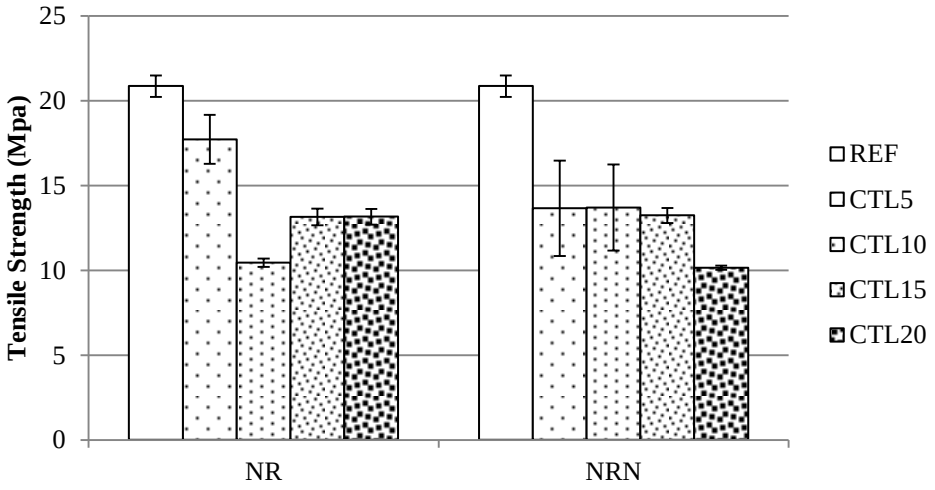


Figure 4.32: Tensile strengths of NR- and NRN-CTL composites

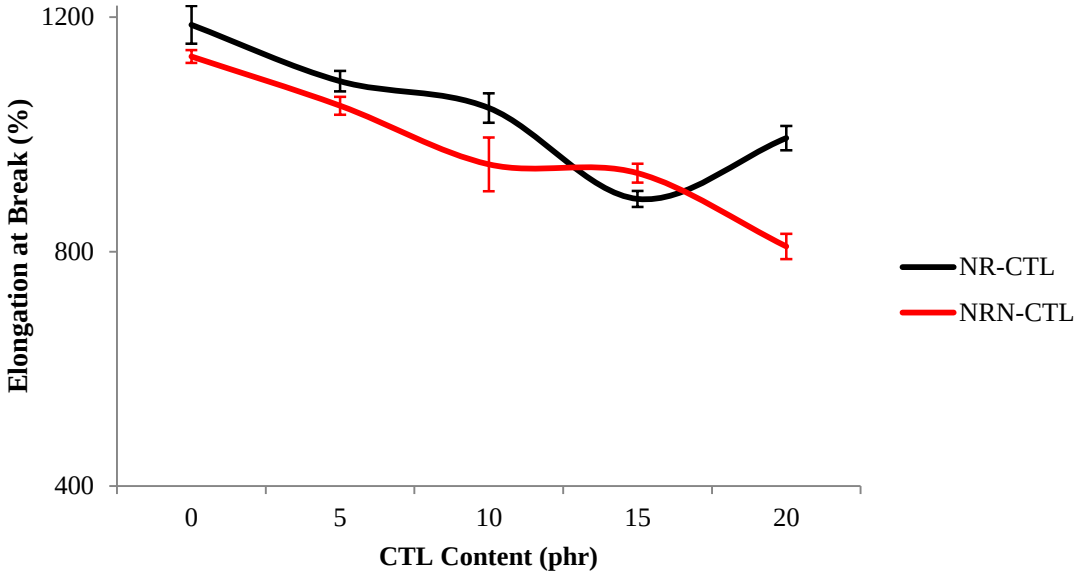
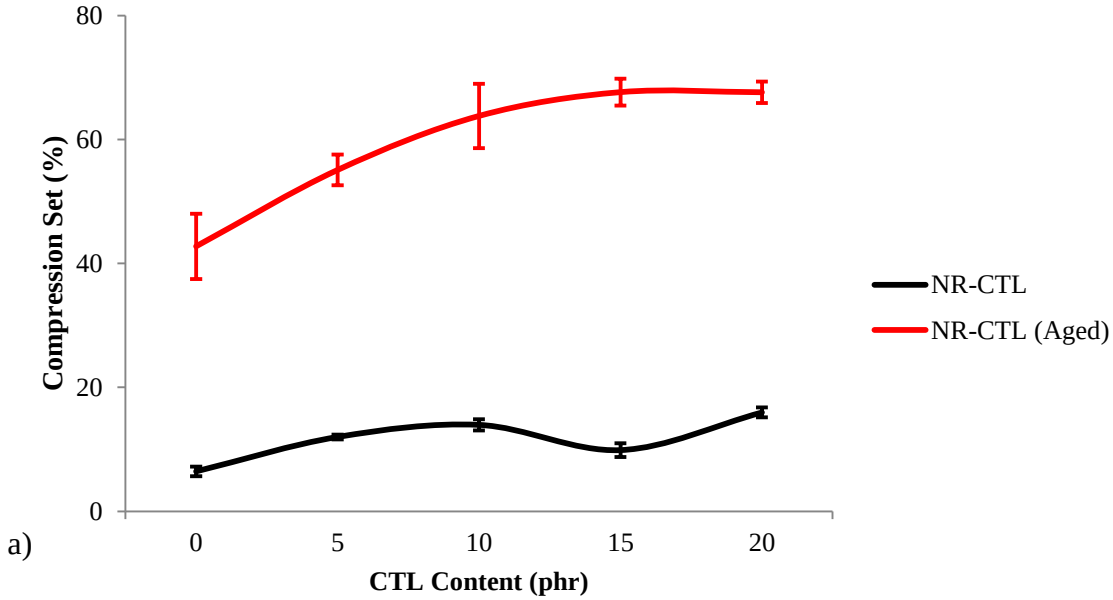


Figure 4.33: Elongations at break of NR- and NRN-CTL composites

4.6.4 Aging properties of neutralized composites

When studied aging properties of composites, neutralized CTL additive did not cause significantly changes on mechanical properties except for tensile strength and elongation at break values. Changes in compression set, hardness, tear strength, and tensile properties of unaged and aged vulcanizates for NR-CTL and NRN-CTL compounds are given in Figure 4.34, 4.35, and 4.36, and respectively.



a)

Figure 4.34: Before and after aging compression set values a) NR-CTL, b) NRN-CTL composites

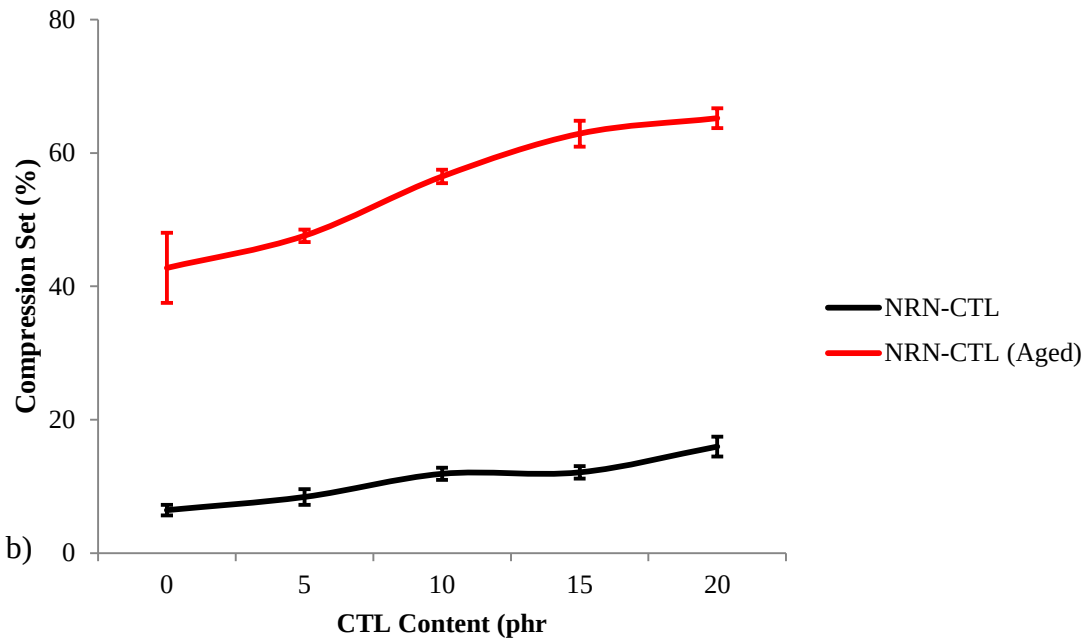


Figure 4.34 (continued): Before and after aging compression set values a) NR-CTL, b)NRN-CTL composites

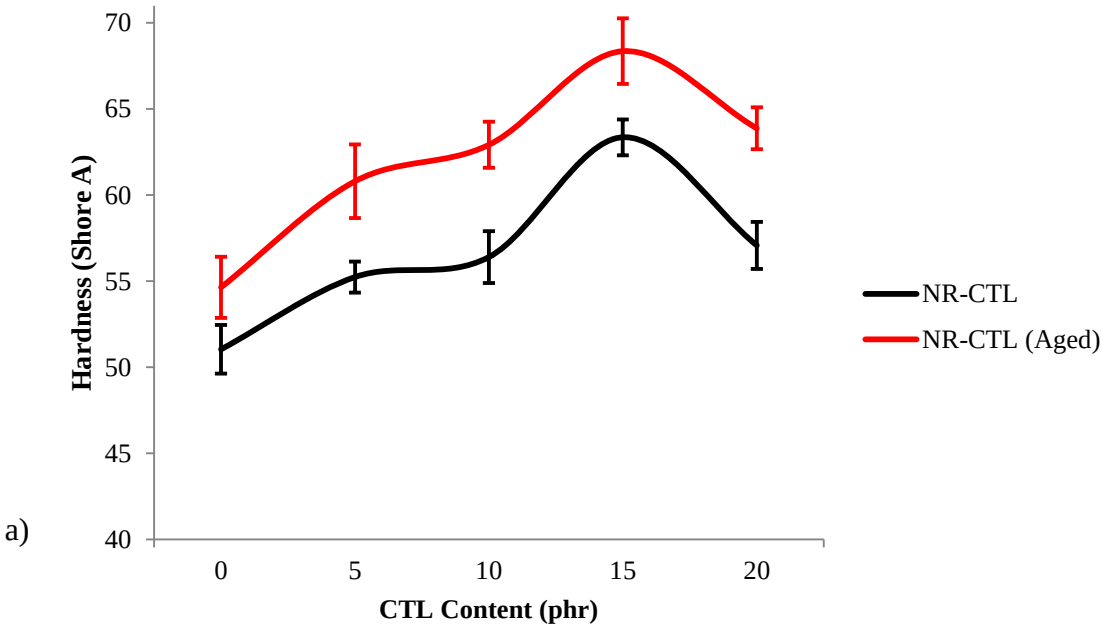


Figure 4.35: Before and after aging hardness values of composites a) NR-CTL, b) NRN-CTL

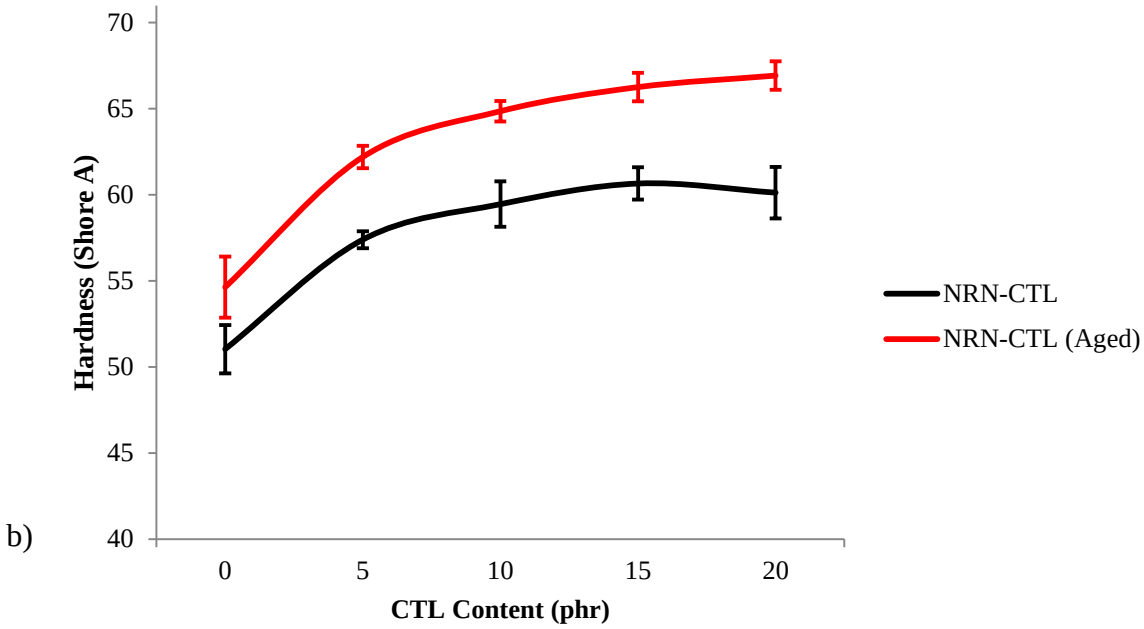


Figure 4.35 (continued): Before and after aging hardness values of composites a) NR-CTL, b) NRN-CTL

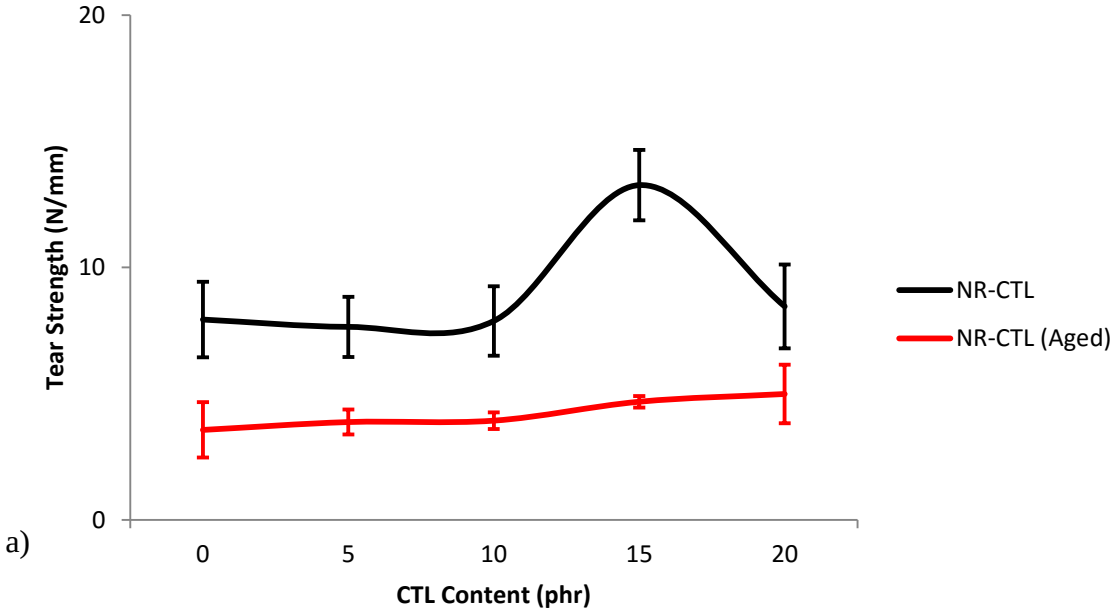
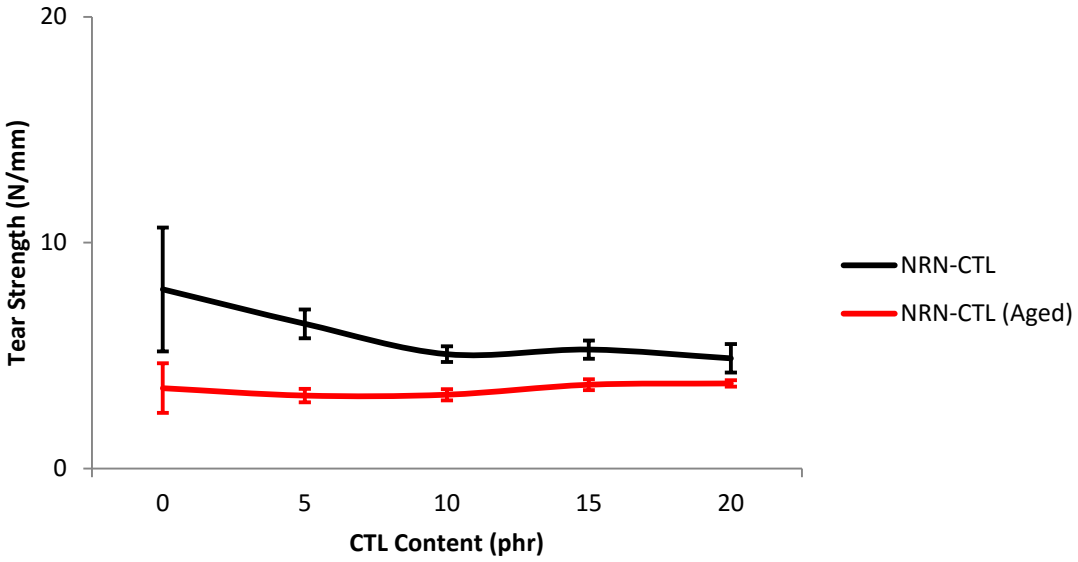


Figure 4.36: Before and after aging tear strength values a) NR-CTL and b) NRN-CTL composites



b)

Figure 4.36 (continued): Before and after aging tear strength values a) NR-CTL and b) NRN-CTL composites

It is obvious from the figures that, neutralization process has not an impressive effect on thermal aging resistance of the NR-CTL compounds, except tensile strength values for CTL containing vulcanizates. This trend may be attributed to lowering the fiber fringes during double grinding in the neutralizing process. Diminished structure of the fiber may cause to decreased ability of fiber providing the tortuous fracture way.

Tensile strength and elongation at break results were given in Figure 4.37 and 4.38.

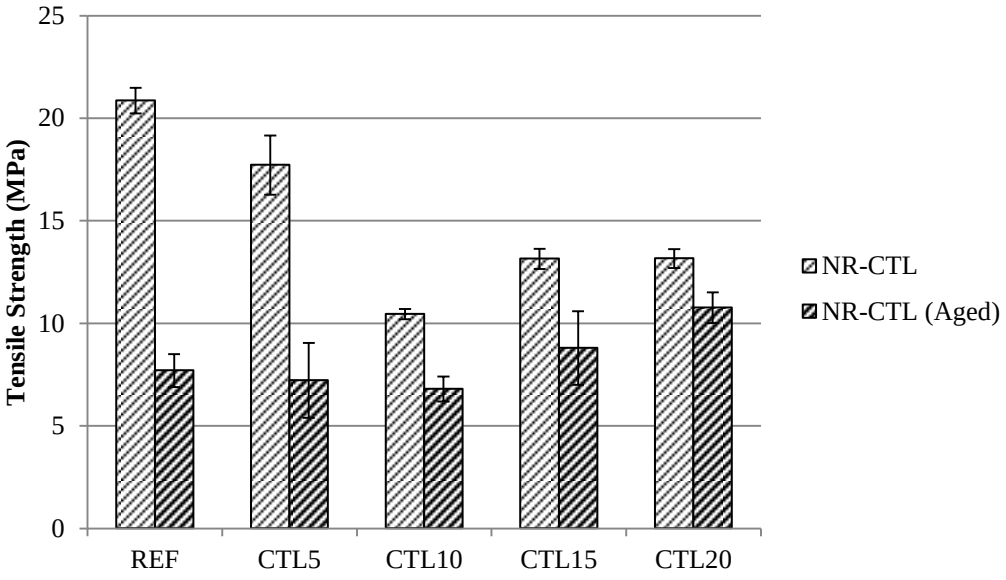


Figure 4.37: Before and after aging tensile strength values a) NR-CTL, b) NRN-CTL

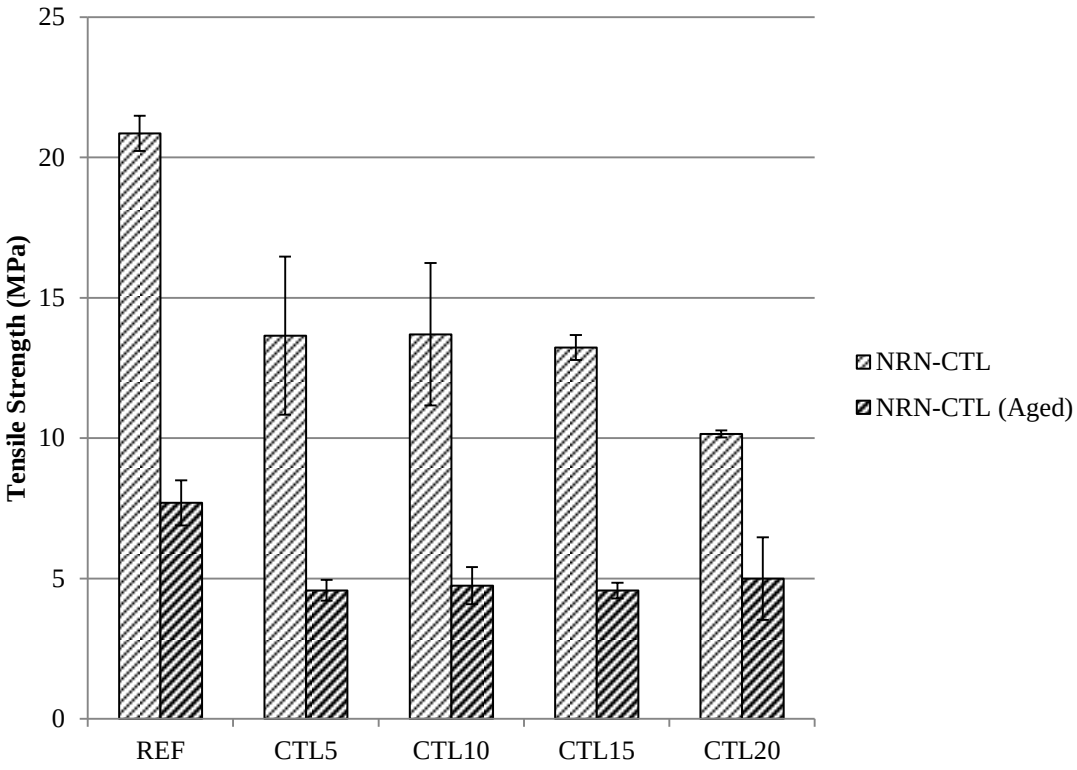


Figure 4.37 (continued): Before and after aging tensile strength values a) NR-CTL, b) NRN-CTL composites

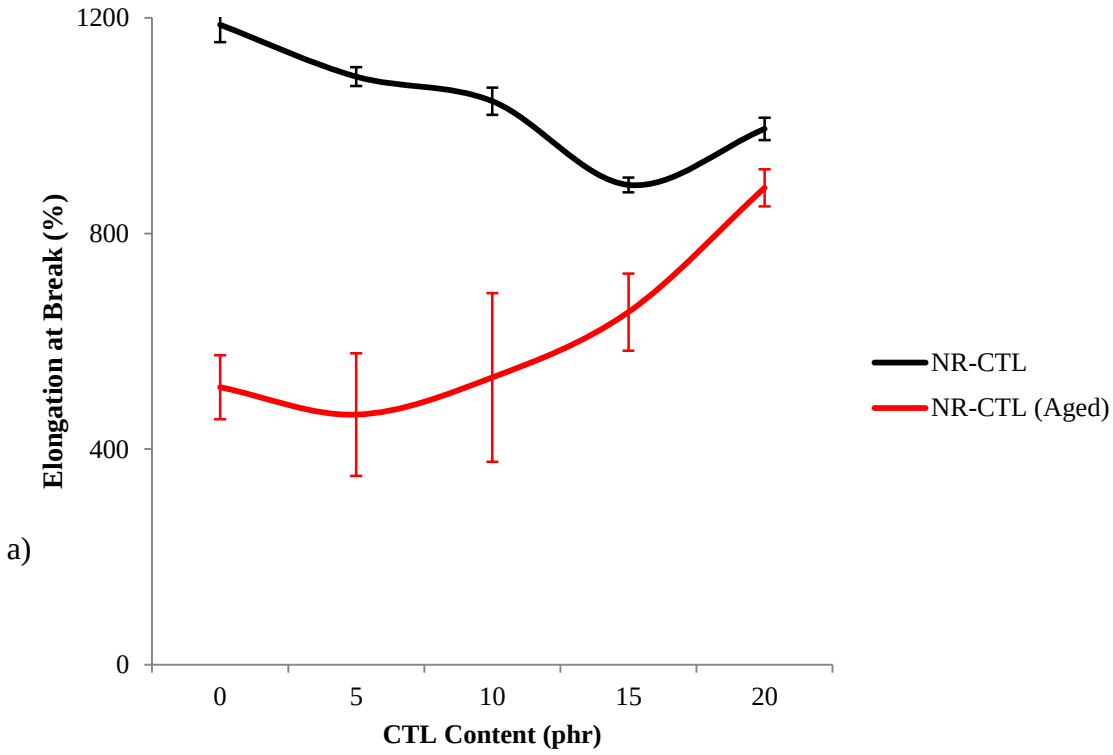


Figure 4.38: Before and after aging elongations a) NR-CTL and b) NRN-CTL composites

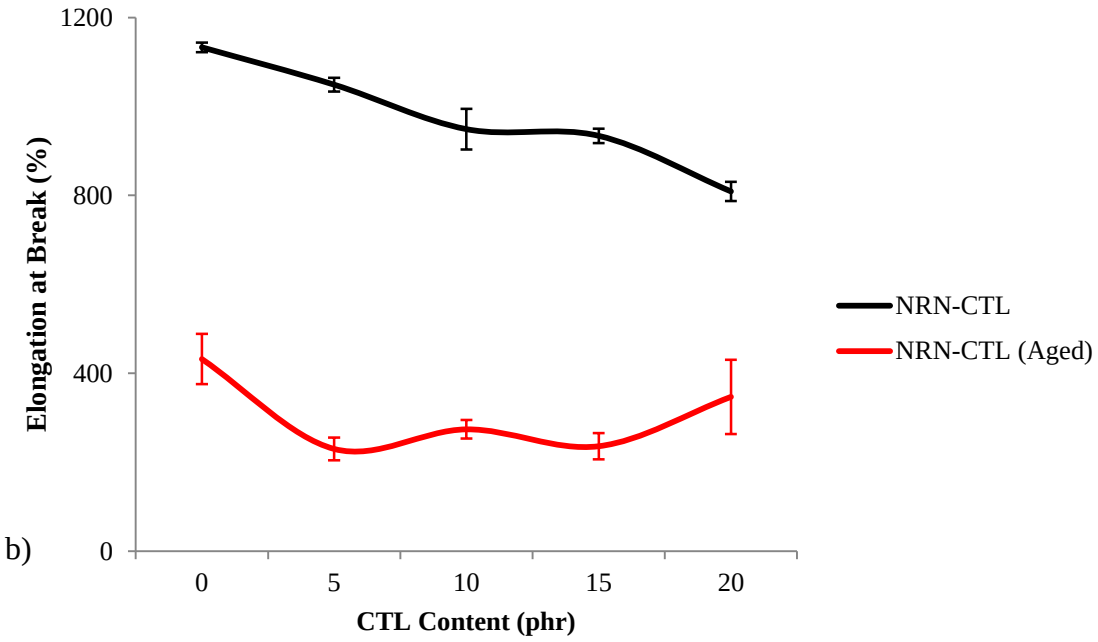


Figure 4.38 (continued): Before and after aging elongations a) NR-CTL and b) NRN-CTL composites

5. DISCUSSIONS

In this thesis, chrome tanned leather (CTL) particles were added into NR, SBR and NR/SBR based compounds before and after neutralization. Mesh size range of CTL was seen changing between 500 and 2000 μm (77.6 wt.-%). CTL was dried in an oven to remove moisture before adding to compounds. The ingredients were compounded in a lab-size banbury mixer then homogenized and layered in a two-roll mill. Chrome tanned leather was investigated as a filler in rubber compounds. Rheological, thermal and mechanical properties were studied before and after 70 ^{o}C and 70 hours aging and the effect of neutralization of CTL on NR based composites was also studied.

Adding CTL to different rubber compounds caused different effects on properties of polymers. DSC curves showed that the ΔH_c values of NR-CTL composites increased with CTL loading. However for SBR-CTL and NR/SBR-CTL composites, ΔH_c values decreased with CTL loading and the curing peak temperatures of all kind of rubber compounds were seen around 160 ^{o}C hence the temperature was chosen for all compounds during rheological test. As seen from the rheometer results there is no significant change on maximum or minimum torque values of NR-CTL compounds with increasing CTL loading. For SBR-CTL compounds M_H values decreased and also an increment on M_L values was observed. A decrement was seen on M_H values of NR/SBR compounds by CTL loading. Slightly increment has been observed on M_L values of NR/SBR-CTL compounds. Maximum and minimum torque (M_H) values provide information about vulcanization characteristic and crosslink densities of the elastomeric compounds. Scorch times of all kind of compounds were shifted earlier with increasing CTL content also t_{90} values decreased by adding chrome tanned leather scraps. This might be due to three dimensional crosslink structure of leather.

Mechanical properties of the composites were studied. The addition of CTL with various ratios into NR, SBR and NR/SBR caused different consequences. Abrasion loss of NR did not change, but the values of SBR and NR/SBR increased with CTL loading. Compression set values showed that increasing CTL content caused an increment on permanent deformation of polymer. The hardness values of NR- and NR/SBR-CTL composites increased with CTL content but the values of SBR did not significantly changed. CTL did not contribute to tear strength of NR based

composites. The best contribution of leather scraps to tear strength was observed for SBR- and then NR/SBR-CTL composites. As compared tensile strength of composites, CTL caused a decrement on tensile strength of NR-CTL composites. On SBR- and NR/SBR-CTL composites, chrome shavings did not have any effect on tensile strengths. CTL also decreased elongation of NR- and SBR-CTL composites. This might be due to non-elastic nature of leather.

Residue amount of NR- and NR/SBR-CTL compounds was decreased by adding CTL, but no effect of CTL was seen on SBR compounds on TGA results.

Aging properties of rubber-CTL composites were also investigated. In compression test which measured permanent deformation on polymer, showed CTL did not neither enhance nor decrease thermal aging resistance of NR-CTL composites however in SBR and NR/SBR based composites permanent deformation increased with CTL loading. In hardness test results, CTL did not enhance aging resistance of NR- and SBR-CTL composites but NR/SBR-CTL composites were more durable against thermal aging. Leather incorporation did not enhance tear strengths of NR- and SBR-CTL composites on the contrary in the literature but increased NR/SBR-CTL composites` tear strengths against aging. As compared tensile strengths and elongation at break values before and after aging, thermal aging resistance of NR based composites was increased by CTL content but the leather additive was not effective in SBR- and NR/SBR-CTL composites.

In addition acidic nature of leather was neutralized by 1% ammonium solution and rheological, mechanical and thermal properties were studied for NR based composites. An increment was seen at ΔH_c values of the composites hence it might be increased crosslink degree of the composites. Abrasion resistance was decreased by CTL content. Permanent deformations of NR based composites was decreased by neutralization at 5 and 10 phr of CTL then increased. Hardness values of composites were increased by neutralization process it might be due to increasing crosslinking. Tear strengths of the composites was lowered by neutralization. Same situation was seen as compared tensile strength values of composites. When evaluated elongation at break values of composites, neutralization process did not affect the values until 15 phr then elongation of composites decreased.

The effect of neutralization on aging properties of NR based composites was investigated. Neutralization did not affect changing of compression and hardness values after thermal aging. In tear results showed neutralization enhanced tear strength slightly with increasing CTL content. However tensile strength and elongation at break values were lower than untreated NR-CTL composites.

Neutralization process did not have any effect on TGA results of composites.

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